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(54) Title: REMOVAL OF CONTAMINANTS FROM WASTEWATER

(57) Abstract

A method of treating wastewater containing hard cations to remove contaminants therefrom, comprises forming a precipitate of at least one insoluble soap in situ by the reaction of hard cations with well dispersed fatty acids or fatty acid salts, and removing the precipitate, said precipitate containing at least a portion of at least one contaminant.

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## REMOVAL OF CONTAMINANTS FROM WASTE WATER

TECHNICAL FIELD

5 This invention relates to the treatment of waste water in order to reduce the level of contaminants therein and to produce environmentally acceptable products.

Contaminants removable from water by the process of the invention include metals such as lead, copper, iron, manganese, cadmium and aluminium, organic contaminants such as benzene, aniline, cyclohexane, acrylonitrile, kerosene and petrol, and also anionic contaminants such as sulphate, phosphate, chloride, fluoride, nitrite, arsenate, arsenite, selenate, selenite, chromate, and organic anionic species such as oxalate and tartrate, and organo-sulphonates.

10 The invention is also effective in removing materials that contribute to biological oxygen demand (B.O.D.) and/or chemical oxygen demand (C.O.D.).

15

SUMMARY OF THE INVENTION

20 The invention provides a method of treating waste water to remove contaminants therefrom, which comprises forming a precipitate of at least one insoluble soap in situ and removing the precipitate, said precipitate containing at least a portion of at least one contaminant.

25 In one aspect the process of the invention involves the formation of insoluble soaps in situ by the reaction between hard cations such as calcium and magnesium with well dispersed fatty acids or fatty acid salts such as the sodium salts of short chain saturated fatty acids ( $C_8$ - $C_{14}$ ) or long chain unsaturated fatty acids ( $C_{15}$  to  $C_{22}$  e.g.  $C_{18.1}$ - $C_{18.3}$ ). Long chain saturated fatty acids, for example stearic acid, may also be employed. Sodium oleate is the preferred fatty acid salt for use in the process of the present invention.

30

We have unexpectedly found that formation of a precipitate by addition of a fatty acid or fatty acid salt to a contaminated water in the presence of a hard cation under alkaline conditions has the effect of not only removing the hard cation, but also removes other contaminants as well. Although we do not wish to be limited by any hypothetical or postulated mechanism for the observed beneficial effect, we believe that in some manner which is not fully understood, the other contaminants are occluded or otherwise carried down with the precipitate and so removed with it. Removal of the precipitate may be accomplished either by settlement, filtration or flotation. The overall result is that removal of contaminants is accomplished using a sub-stoichiometric amount of reagents, and this represents a significant commercial advantage in the art of waste water treatment.

The process of the invention is superior to previously know methods of waste water treatment not only in economy of reagents, but also in time, as will be apparent from the experimental results reported below.

We have carried out studies using contaminated waste water from the Woodlawn Mine, Tarago, New South Wales, Australia (hereinafter "Woodlawn") and from other sources. These are discussed below under the following headings.

1. Precipitation/Coagulation testwork
2. Reaction kinetics
3. Woodlawn reaction kinetics
4. Sedimentation Testwork
5. Flotation Testwork
6. Removal of Organic Materials, including those which contribute to B.O.D. and/or C.O.D.
7. Removal of anionic contaminants

8. Removal of anionic and organic contaminants using organic bases

9. Reagent Recycling

In the accompanying drawings:

5 Figures 1.1, 1.2 and 1.3 illustrate data obtained in the sedimentation testwork study (4).

Figures 2.1 to 2.6 illustrate data obtained in the reaction kinetics study (2).

10 Figures 3.1 to 3.9 illustrate data obtained in the Woodlawn reaction kinetics study (3).

Figure 4.1 is a flowsheet illustrating an embodiment of the invention utilising reagent recycling as discussed in study (9).

15 Figure 5.1 illustrates a further embodiment of the invention.

#### BACKGROUND OF THE INVENTION

20 The problems associated with acidic mine waste water in terms of water storage, water treatment and usage and mine rehabilitation are well documented and in this connection reference may be made to the detailed papers and discussions in the proceedings of the International Symposium Lisboa 90 "Acid Mine Water in Pyritic Environments" (September 1990).

25 The approach detailed below aims to treat waste effluent waters, such as those found as acidic mine water, in a chemically efficient and cost effective manner to produce a high quality dischargeable water and a solid sludge that may be recycled or disposed of in an  
30 environmentally acceptable package.

The example below indicates the quality of water that can be treated by the process - this particular water is produced as acid mine water at the Woodlawn mine at Tarago, N.S.W., Australia.

TABLE 1. - WASTE WATER COMPOSITION (ppm)

<u>Element or ion</u>	<u>North Dam Water</u>	<u>South Dam Water</u>	<u>Lake Rex Water</u>
Cu	100	77	41
Pb	1.5	1.4	0.2
Zn	3000	1860	737
Fe	200	92	41
Cd	12	9.3	5.0
Mn	130	84	31
Na	300	370	82
K	3	2	1
Al	610	355	170
Ca	400	390	140
Mg	1700	920	330
SO <sub>4</sub>	16900	9420	3880
Cl	200	120	550
pH	3.1	3.2	3.3

# 1. PRECIPITATION/COAGULATION TESTWORK

## Background

The generation of "hard" soaps in acid mine water effluents has been studied in an effort to accomplish the removal of heavy metals by occluding them into the precipitate formed between hard cations (such as calcium and magnesium) and carboxylate. These hard soaps are generated by the formation of insoluble calcium and magnesium soaps either of the well dispersed fatty acid or of the liquid fatty acid salt, for example the sodium or potassium salts of short chain saturated fatty acids ( $C_8$ - $C_{14}$ ) or long chain unsaturated fatty acids ( $C_{15}$ - $C_{22}$ , e.g.  $C_{18.1}$ - $C_{18.3}$ ). Long chain saturated fatty acids may also be employed. The work conducted to date has focussed on the use of commercial sodium oleate as the reagent. This is primarily due to its unequalled effectiveness as a "blanket" removal reagent for a range of metal elements. Sodium oleate is also easily handleable as a dilute liquid.

Examination of the mechanism of precipitation has been necessary due to the variation in performance of the precipitation as applied to heavy metal removal from acid mine waters. Irregularity in the matrix of the feed water was observed in testwork to have altered the metal removal capabilities of the coagulated precipitate. S/L separation performance for the generation of a clean dischargeable water was also observed to be effected.

The objective of this testwork was to characterise the reaction conditions necessary to effectively remove the heavy metals cost effectively whilst yielding a water of suitable quality for recycle or discharge. This was with particular reference to initial calcium concentration required prior to fatty acid addition and the type and rate of insoluble sludge formed.

Laboratory Procedure

5 A "live" sample of water from a mine tailings dam was used for all the testwork conducted. Analysis of this water sample showed the calcium concentration to be around 30ppm. Upon reagent addition to this sample, a cloudy solution was observed. This was unlike previous observations with mine water samples where a precipitate was seen to form and then coagulate to form a definitive solid phase. Analysis of previous water samples showed the calcium concentration to be around 150ppm.

10 The calcium concentration prior to fatty acid addition was noted to affect the solid phase characteristics of the precipitate formed in solution and hence the ability of the precipitate to effectively isolate the metal contaminants present in the water into a handleable sludge.

15 Based on these initial results, a more complete study of the calcium concentration, reagent requirements and heavy metal removal capabilities was required to fully understand the basis under which the precipitation was most cost effective.

20 To investigate these reaction criteria, a fraction of the "live" water sample was "spiked" with calcium sulphate. This effectively increased the soluble calcium level from 30ppm to 150ppm. This stock solution was then diluted to give varying calcium concentrations from 150ppm to 30ppm. These solutions were measured for calcium concentration by atomic absorption spectroscopy (AAS).

25 Varying quantities of the sodium oleate were then added to react with a fraction of the calcium ions present. The precipitate type and coagulation were noted. The precipitate was then filtered and the calcium concentration



of the filtrate measured by AAS.

New samples of the calcium solutions were then "spiked" to give a resultant 2ppm lead concentration. The oleate additions were repeated and the resultant precipitates filtered and the filtrate lead concentrations measured by AAS.

From these results, the optimum calcium concentration and sodium oleate reagent addition could be quantified to give the best result in terms of precipitate formation/coagulation. This could then be related to the stoichiometry required of reaction between the calcium and oleate ions. The effect on metal removal from the system could also be characterised in terms of the stoichiometry of the reaction.

#### 15 Laboratory Results

The results of the testwork can be seen outlined in the Table below.

Init[Ca] (ppm)	% Stoich.	Final[Pb] (ppm)	Observation
150	20	< 0.1	Precipitate. Coagulated quickly
110	30	0.2	Precipitate. Coagulated slowly
77	48	1.0	Precipitate. No coagulation
35	95	-	Precipitate. No coagulation
110	10	< 0.1	Precipitate. Coagulated quickly
75	35	0.1	Precipitate. Coagulated v. slow
38	50	-	Precipitate. No coagulation
110	4	< 0.1	Precipitate. Coagulated with stirring
72	10	0.2	Precipitate. Coagulated with stirring
35	20	0.4	Faint precipitate. No coagulation

Conclusions:

Based on the results, the following conclusions can be made.

- 5           1.       The initial calcium concentration in solution is important in terms of the performance of the coagulation step. Precipitates will be formed no matter what the stoichiometry relationship.
- 10           2.       The amount of free calcium in solution following the completion of the reaction with the oleate anion is important to the coagulation step. By calculation a residual calcium concentration of 90 to 100 ppm gives the best coagulation results in terms of residence time.
- 15           3.       The degree of coagulation in turn effects the quantitative removal of the metal ion, in this case lead, from the aqueous solution. In the case where the coagulation has occurred quickly and a distinct solid phase been formed, the lead removal is to within 0.05ppm. Lower levels of calcium at a similar reaction stoichiometry show slower coagulation tendencies and do not remove the heavy metals to the levels required.
- 20
- 25           An operating system for the removal of lead in the water described would require an initial calcium concentration in the order of 110 - 150ppm prior to addition of sodium oleate. To effectively lower the lead concentration from 2.0ppm to 0.05ppm and below, a sub stoichiometric addition of sodium oleate at 10 - 20 molar % of the initial calcium concentration is sufficient to occlude the heavy metal cations.
- 30

It appears that the calcium oleate formed in solution and the coagulation process are both important to

the removal of the lead ions from solution. The presence of the calcium ions appears to have the unexpected effect of minimising the reagent requirements for the metal removal. This is unlike conventional precipitation techniques which rely on the total precipitation of individual metal species from solution.

## 2. REACTION KINETICS AS APPLIED TO TREATMENT OF WASTE WATERS

With the success of the removal of heavy metal cations from waste waters using sodium oleate, a more detailed laboratory study was required to examine the factors surrounding the engineering requirements and economics of the process.

Factors that required evaluation were reagent addition, residence time and the initial concentration of heavy metals in the feed water under continuous flow reaction conditions. The initial water system chosen for study contained only the lead ion.

### Laboratory Procedure

The objective of the testwork was to follow the concentration of lead over time under differing reaction conditions of initial lead concentration and reagent addition.

To conduct the work, a "live" water sample from a mine site was used for the duration of the testwork. It was at a pH of 8 - 9.

From previous batch experimental work, a calcium concentration of 150ppm prior to reagent addition was required to properly facilitate the precipitate formation. Therefore, all experiments were conducted under conditions of 150ppm free calcium concentration.

Initial lead concentrations of 0.25 and 0.5 ppm were used. These represented discharge levels that are considered excessive at the site in terms of license

requirements. The lead was increased in concentration by the addition of a suitable quantity of lead standard.

The reagent addition ranged from 0.06 - 1.00 g/L sodium oleate added as a 5% active solution.

5 The reaction was conducted in a two litre beaker gently agitated by a magnetic stirrer to ensure adequate mixing of the reagent in the aqueous system.

Sub examples of the reaction liquor were taken at minute levels over a 10 minute time frame. These samples  
10 were then filtered and analysed for lead by AAS. Considering the close proximity to the limit of detection for AAS, cross checks were conducted using ICP.

The results from the tests were then expressed as a function of addition over the ten minute interval at a  
15 set initial lead concentration.

#### Laboratory Results

All testwork results are represented in Figures 2.1 to 2.6.

The data is shown as lead concentration over time  
20 at differing initial lead concentrations at a constant sodium oleate dose. The required discharge level is also indicated on each curve at 0.05 ppm.

Figure 2.1 shows the reagent performance at 0.06 g/L reagent addition. This level of reagent addition is  
25 not sufficient for lead removal to the required levels. This is due to the levels of precipitate formed in solution not being adequate for the occlusion of the contaminant ions into the precipitate.

By doubling the reagent dosage to 0.12 g/L as  
30 shown in Figure 2.2, the required lead level suitable for discharge is reached. This was achieved after a residence time of three minutes. It is of interest to note that the level of lead remaining in solution remains static

after the three minute time interval, similar to that in Figure 2.1.

Similarly for Figures 2.3 - 2.5, the desirable lead discharge level is reached after a three minute time period. The final lead level reached at a reagent dosage of 0.24 g/L is comparatively lower than that at 0.12 g/L. The final result is not affected by increasing the reagent addition beyond 0.24 g/L to 0.50 g/L as is seen in Figures 2.4 and 2.5.

At an addition level of 1.0 g/L, the residence required to achieve the result at a dosage of 0.24 g/L is increased to around 10 minutes. This is depicted in Figure 2.6. This may be due to the decreased free calcium concentration in the reaction solution caused by the formation of larger quantities of calcium oleate. The lower free calcium concentration may take a longer time to effectively coagulate the precipitate and hence effectively remove the contaminant cation from the water.

The final lead concentration achieved is not dependent on the initial lead concentration in the process water. At initial lead concentrations of 0.25 and 0.50 ppm, the final lead concentration is reduced to levels in the order of 0.02 ppm. The residence time required to achieve this result is not altered as a consequence of the initial lead concentration nor is it affected by the reagent addition level up to 1.0 g/L. The removal of other heavy metals was also measured and was shown to be below discharge limits.

#### Summary

The above results indicate that under laboratory conditions, a level of 0.24 g/L sodium oleate is required to reduce the lead concentration from 0.5 ppm to 0.02 ppm. This result was achieved after a residence time of three minutes in the laboratory reactor

system.

### Conclusions

Reagent requirements of a maximum of 0.24g/L with a residence time of 5 minutes are required to effectively lower the lead concentration to the required lower limit of 0.05ppm.

In comparison to previous results from batch testwork, the result achieved from the testwork is a vast improvement in terms of reagent dosage where the reagent requirements were around 1.0 g/L.

The time frame under which the reaction must take place is 40% less than anticipated for a successful result to be achieved.

The lead removal was also complete after one pass through the system and therefore does not require a second stage treatment to achieve dischargeable levels.

### 3. STUDY OF CATION REACTION KINETICS IN THE TREATMENT OF WOODLAWN WASTE WATER

Following the success of results from examining lead removal, testwork was similarly conducted on the Woodlawn process waters containing a complex matrix of metal ions to examine results obtainable under similar reaction conditions.

The testwork examined a series of elements that must be reduced in their concentration before the water can be discharged successfully off the site at Woodlawn.

### Laboratory Procedure

A procedure similar to that carried out in previous tests was conducted. This involved following the reaction as a function of concentrations of certain metal elements over time at a fixed reagent addition.

A "live" water sample produced from the Woodlawn

system was used for the experiments. This solution did not require an increase in calcium concentration as had been necessary for the above system as the calcium concentration was at 400 ppm.

5           Figure 3.9 indicates the initial feed metal concentrations prior to and after pH adjustment with  $\text{CaCO}_3$  and  $\text{Na}_2\text{CO}_3$  before being used as the feed source for the kinetics experiments.

10           The reaction was carried out in a two litre beaker that was gently agitated by a magnetic stirrer. Sub samples were taken at minute intervals over a ten minute period and filtered before being analysed by AAS.

          A total of ten elements were measured to determine what the "rate determining" ion was in a more complex system.

15           Laboratory Results

          The results from these tests are shown in Figures 3.1 - 3.8.

20           Figure 3.1 indicates results from examining residual copper concentration in solution as a function of differing levels of reagent addition. Copper concentration for water discharge must be 1ppm or less by Government regulation. From Figure 3.1, the initial concentration prior to entering the reaction

25           stage was 0.1ppm, well within the concentrations required.

          The results nonetheless still indicate that the residual concentration can be lowered down to 0.03ppm on average at a dosage of 0.5g/L active. In comparison to the previous results, the reagent requirements are a double to

30           achieve a notable reduction in copper concentration.

          Similarly, Figure 3.2 shows the results for residual lead concentration. As for the previous system, a residence time of approximately three to four minutes is

required to achieve the target lead concentration of 0.05ppm. This is achieved at a dosage of 0.5 g/L unlike the requirements to achieve the same result as from previous tests at 0.25 g/L.

5 It is concluded that owing to the total metal concentration present in the Woodlawn sample, an increase in reagent requirements is required to achieve the same result.

10 The time to reduce the concentration to extremely low levels still requires a dosage of 0.5 g/L but only requires a residence time of approximately one minute.

Figure 3.4 shows the result for studying the residual iron concentration. A short residence of one to two minutes at a dosage of 0.25 g/L achieve the result required of being below a concentration of 0.3ppm.

15 The residual concentration of cadmium in the reaction system reveals a more complex picture. At a dosage of 0.5 g/L a minimum residual concentration is achieved after a period of four to five minutes. This however does not satisfy the requirements for discharge for the process water. Figure 3.8 shows that a second reagent dosage of 0.5g/L is required to lower the final cadmium concentration to within acceptable discharge levels.

20 This observation is similar to the results found for residual manganese concentration as shown in Figure 3.7. Manganese also requires a second reagent addition of 0.5 g/L to achieve the required standard as shown in Figure 3.8 of 0.05ppm.

25 Aluminium levels as depicted in Figure 3.6 are also suitably reduced under the same reaction conditions of 0.5g/L reagent addition with a residence time of three to four minutes.

### Conclusions

Based on the observed results, the cation which



presents itself as the "rate determiner" is that of cadmium. The requirements to achieve the discharge concentration see a two pass system with each reaction consuming 0.5 g/L sodium oleate at a resident reaction time of three to four minutes.

All other cations in the Woodlawn system would meet the discharge requirements if the above kinetics are satisfied in the cation removal step.

In a more complex matrix of contaminants, a larger volume of reagent may be required to effectively remove contaminants to required levels.

#### 4. SEDIMENTATION TEST WORK

This study aimed to develop a suitable technique for the isolation of the precipitate formed in the removal of a wide variety of contaminants from waste waters. This would allow for the isolation of the clean water with a handleable sludge that could be disposed of or recycled.

In this particular study the precipitate formed in situ occupied a volume of between 0.25 and 0.5% by weight of the total solution, exhibited hydrophobic properties and had an S.G. of around 1.02. The hydrophobic nature of the material gives it a tendency to float upon contact with entrained air. However, if air entrainment is minimised, the material will slowly settle in water. The concept of settling or sedimentation was therefore examined owing to the natural tendency of the bulk of the particles in the aqueous system to settle.

Free settling of this type of precipitate would normally require vessel(s) of a large surface area owing to the very low settling rates of 0.5 metres per hour. As previously indicated, a fraction of the precipitate formed has a tendency to float and does not allow comprehensive free settling of the precipitate to take place such that

the water produced is of suitable quality.

Operating practices adopted in other industries (e.g. pulp and paper) use clays as a substrate to adsorb hydrophobic material hence allowing the bulk material formed to settle at accelerated rates, minimising the required surface area for settling.

This technique was initially examined for this system with clays, in particular bentonite. The addition of bentonite was successful in settling the precipitate at accelerated rates with a resultant clear supernatant. However, the physical characteristics of the bentonite made it difficult to handle so alternatives were sought.

Fine crushed pyrite, often found as a mine tailings material, was a convenient material to be used as the adsorbent substrate. This combined oleate/pyrite sludge gave rise to settling rates in the order of 1.5 m/hr with acceptable supernatant clarities.

A "continuous flow" laboratory test was undertaken to conduct tests to examine the suitability of the sedimentation technique.

Industrial sedimentation practices employ the use of thickeners or clarifiers. Thickeners facilitate the concentration of dilute slurries to a pulp of manageable density whilst producing an overflow of clean water or process liquor. Thickener design is varied dependent on the substance being settled and the system it is being applied to.

The unit operation examined for this treatment step was that of a High Rate Thickener (HRT). This unit operates using a much smaller surface area than a conventional thickener treating the same process flow. The HRT also has the advantage of the "sludge bed" principle. In this technique, material reporting into the centrewell is effectively filtered by the settling bed of processed

slurry. This helps to remove finer particles which may not have been effectively treated prior to reporting to the thickener. This technique may also give an extended residence time for the removal of free metal ions in the slurry.

The testwork program examined the parameters effecting performance of the thickener such as overflow clarity and underflow density under differing operating conditions.

#### 10 Laboratory Procedure

A continuous reaction/settling system was assembled to conduct the testwork.

The system comprised two main unit operations, the precipitation reaction and the sedimentation step.

15 The precipitation was conducted in a two litre beaker gently agitated by a magnetic stirrer. Gentle agitation was used to minimise air entrainment in the precipitate slurry whilst ensuring adequate contact of reagent and water. A residence time of five minutes was used for the reaction. The feed flow of contaminated water to, and the water/sludge slurry from the reactor were matched so as to maintain steady state conditions in the reactor.

25 The slurry was then pumped from the reactor at a set rate to the thickener. Addition of pyrite followed by the addition of a dilute flocculant were carried out sequentially in line before the final flocculated slurry was presented to the thickener for settling. The quantities of flocculant and pyrite used were similar to that used in the batch tests.

30 An overview of the reaction sequence is illustrated in Figure 1.1.

The reagents were added as the following activities :

18

Sodium Oleate	5% v/v
Pyrite Slurry	10 % w/v
Flocculant	0.025% w/v

5 The sedimentation was carried out in a high rate thickener unit. The unit had a diameter of 94mm and represented a scaled model of that found in normal operating practice.

10 The lab scale thickener unit allowed for calculation of flow rate per unit area. This was carried out by measuring the overflow launder volume over time. With a set unit area, a common quotient (the rise rate) was calculated. By applying the rise rate to any feed flow, the diameter of the high rate unit required for that application could be calculated.

15 Tests examined varying flow rate to the thickener at a range of pyrite and flocculant addition levels whilst maintaining steady state precipitate conditions. The overflow volume per unit time was then measured while sampling the overflow for the analysis of suspended solids.

20 The suspended solids were filtered and then dissolved in aqua regia before analysing for iron by AAS. The iron concentration was then equated back to the pyrite level in mg/L, pyrite being the major constituent of the tailings used. Underflow samples were collected  
25 simultaneously and their densities measured as percent solids.

The data collected gave indication to the relationships between operating conditions, water quality and estimates of both operating and capital costs for concentration of the precipitate by this technique.

### 30 Laboratory Results

Testwork initially concentrated on establishing the laboratory system to reproduce the results found from conducting cylinder testwork.

Following initial trial runs under operating conditions used in batch tests, the sedimentation technique under continuous flow was found to be consistent with results generated from batch tests.

5       The majority of the testwork was therefore directed on examining the relationship between flocculant, pyrite and feed flow to the laboratory scale thickener.

10       A series of tests were conducted looking at the above parameters and their inter-relationship with each other in the continuous system.

15       Results from these tests are depicted in Figure 1.2. This curve clearly shows the effect of the amount of flocculant added to the precipitate slurry as a function of feed flow and overflow clarity. It should be noted that these tests were conducted at decreasing levels of pyrite from 7 - 1.8 g/L and varying flocculant addition of 10 - 45 ppm. This dilution of pyrite in the feed slurry can be seen in Figure 1.3. A decrease in pyrite concentration in the slurry feed may have given a general increase in the hydrophobicity of the new slurry as the flow increased thus directing a fraction of the fine pyrite to the overflow discharge.

20       At typical settling rates of 1.5 - 2.0 metres per hour, the flocculated slurry from the tests in an HRT of this dimension would not be expected to exceed 500 mL/min feed flow. Results from feed flows at and below 500 mL/min show that the overflow suspended solids levels ranged between 12 - 2ppm (as pyrite).

25       Results from Figure 1.3 show a similar relationship between pyrite added and overflow clarity. A combination of the two curves shows the conditions required to generate the overflow clarities indicated.

### Conclusions

The results have revealed some limitations to employing this technique for the concentration of the precipitate into a handleable sludge.

5 Firstly, water clarity was not considered to be consistent enough for a one step clarification operation to be employed. Therefore, a two stage clarification step would need to be employed to achieve acceptable water clarity. This would limit the application both in space  
10 requirements and economics.

Secondly, the volume of sludges produced would be economically prohibitive owing to the large mass of substrate material required to achieve adequate settling.

### 15 5. FLOTATION TESTWORK

Flotation was an alternative method investigated for separation of the precipitate from the water.

#### Background

20 Solid liquid separation can be achieved by filtration, flotation or sedimentation. Owing to the hydrophobic nature of the precipitate, the precipitate formed has a strong affinity for air bubbles making it particularly suitable for adoption to the flotation process.

25 An investigation into the use of Dissolved Air Flotation (DAF) and conventional flotation was carried out to quantify the performance of these techniques for the removal of the heavy metal containing precipitates.

30 The flotation froth produced was filtered and then recycled to reform the sodium oleate reagent and to produce an aqueous concentrate of the contaminant heavy metals suitable for reprocessing and/or marketing.

The other product namely calcium sulphate produced during the acid hydrolysis of the precipitate can

be used as a source of Ca for the feed water if necessary.

#### A: DISSOLVED AIR FLOTATION

##### Background

5           Dissolved Air Flotation is a method of water  
purification commonly used in the water treatment industry.  
It relies on the "precipitation" of small bubbles to  
collect small particles of suspended matter from solution  
following the injection of pressurised water that has high  
10       concentrations of dissolved air in it.

A DAF unit was obtained which consisted of a  
pressurisation cell connected to an open flotation cell of  
capacity about 1.6 litres.

15       Water was introduced into the pressurisation cell  
and nitrogen used for increasing the pressure in the cell  
to 500 kPa.

Known volumes (100, 200, 500 & 900 mL) of the  
pressurised water were then injected into the base of the  
flotation cell where the nitrogen "precipitated" in  
20       solution in a fine array of bubbles thus providing the  
mechanism to float the precipitate. Both the surface  
concentrate and cell water were then sampled and assayed  
for solids concentration.

##### Experimental

25       A 1000 mL sample of the slurry was used with  
pressurised volumes of 200, 500 & 900 mL being injected.  
The concentrate was sampled after 3, 5 & 10 minute  
intervals, the cell water was sampled immediately  
thereafter. The samples were filtered through GF/C filter  
30       papers, dried at 110-120°C and weighed.

##### Results

A feed density for the tests was measured to be  
0.33g/100mL of solution (0.33% solids).

The results are outlined in tabular form below.

The precipitate was adequately separated from the bulk water utilising the DAF technique. A residence time of 10 minutes was required to give the required water clarity.

5

To achieve this result a 90% recycle of the water volume was required to achieve a high quality water clarity. A limiting factor to the employment of this technique is the volume of the recycle water that is required. This means the potential operating plant would be quite sizeable to effect the separation adequately.

10

However, if water clarity is a minor factor in terms of final water quality, the DAF process is suitable as a method of solid/liquid separation for the precipitate sludge.

15

The experiments have concluded that the DAF technique is effective for removal of the precipitate from the bulk water while generating a water of suitable clarity.

20



a) 1000 mLs feed + 200 mLs N <sub>2</sub> H <sub>2</sub> O		
Time after inject. (mins)	Conc. (wt% CaO <sub>l</sub> )	Water (wt% CaO <sub>l</sub> )
2	11.0	0.09
5	1.40	0.04
10	14.5	0.03
b) 1000 mLs feed + 500 mLs N <sub>2</sub> H <sub>2</sub> O		
Time after inject. (mins)	Conc. (wt% CaO <sub>l</sub> )	Water (wt% CaO <sub>l</sub> )
2	11.5	0.07
5	14.0	0.03
10	15.0	0.02
c) 1000 mLs feed + 900 mLs N <sub>2</sub> H <sub>2</sub> O		
Time after inject. (mins)	Conc. (wt% CaO <sub>l</sub> )	Water (wt% CaO <sub>l</sub> )
2	10.0	0.07
5	14.5	0.02
10	15.3	0.01

Observations made in these experiments did conclude that the small bubble size generated by the DAF technique was not ideal for the precipitate separation from the bulk solution and that a larger bubble size may be more appropriate for the separation required.

## B: CONVENTIONAL FLOTATION

### Background

Conventional flotation utilises much larger bubbles in the separation of hydrophobic particles from a bulk solution.

Initial experiments were conducted after generating the precipitate in a separate reaction vessel prior to flotation.

The conventional flotation system has some advantages over DAF. High pressure air is not required and the bubble size generated can be controlled by system controls. High flow rates do not require large amounts of floor space, particularly where the slurry has the characteristics displayed by the precipitate.

Using the flotation tank as a combined reaction vessel/float cell has the advantage of being able to carry out the reaction in a simple batch operation in the laboratory to obtain results that would be directly correlated to a pilot operation.

#### Experimental

A contaminated water sample containing soluble heavy metals was added to the laboratory flotation cell followed by the required amount of reagent. The cell was then agitated at low speed for a period of 2 - 3 minutes before increasing the speed and introducing air into the system for a period of 1 minute. A sample of the froth was then collected.

Flotation then proceeded under these conditions for a period of 5 minutes. The total froth was then "screened" to improve the solids density. The remaining water was sampled for suspended solids analysis.

#### Results

Sample	Feed Solids (%)	Froth Density (%)	Water Solids (%)
NDW - Stage 3	0.62	17 - 22	< 0.01
Hellyer	0.25	15 - 20	< 0.02

The experiments were repeated and the results reproducible within the range specified. The remaining water was analysed by ICP for heavy metal elements with levels below those required for licensed discharge.

Conclusions

Based on the experimental results, obtained from tests conducted using both DAF and conventional flotation, it would appear that the conventional flotation has advantages.

The solids density of froth from the conventional cell is around 5% greater than the DAF unit with a 50% shorter residence time to achieve this result. The suspended solids level in the water that would be discharged is also low with a level less than 0.01%.

6. REMOVAL OF ORGANIC MATERIALS FROM WASTE WATERS

The process of the invention is also effective for the removal of organic materials from waste waters. The following experimental work relates to this aspect of the invention.

These organic materials included oils and partially water soluble organics.

Procedure

Using a standard Denver flotation cell a series of tests were carried out as follows:

Volume of Water (tap water - pH neutral) = 1200mL

Addition 1 - Organic contaminants @ 420 - 430 ppm

Benzene

Aniline

Cyclohexane/Acrylonitrile

Kerosene/Petrol

Addition 2 - Provide Calcium source

1.0gm Calcium Chloride dissolved in float cell

Addition 3 - With air flow off add 10 mL of 5% sodium oleate.

Homogenise for a period of five minutes using a slow rotation speed. Increase the rotation speed, turn on the air and recover the precipitate plus absorbed organic's by flotation; 2 - 3 minutes.

### Results

After collecting the concentrated Ca Oleate sludge following flotation, the remaining water was analysed for the listed contaminants.

Results are as follows;

Organic Contaminant	Residual Concentration
Benzene	Removed to < 1ppm
Aniline	Removed to < 1ppm
Cyclohexane/Acrylonitrile	Removed to approx. 1ppm
Kerosene/Petrol	Removed to < 1ppm

### Conclusions

Based on these short term tests, the Ca oleate precipitate and the mechanism of precipitation allow for the quantitative removal of organic based contaminants from waste waters.

### REDUCTION OF BIOLOGICAL OXYGEN DEMAND (B.O.D.)

The following data relate to the process of the invention as applied to removal of materials contributing to B.O.D.

Background

The reduction of B.O.D. and suspended solids in effluent waters is of importance to many industries.

5 B.O.D. is measured by many Government sewer operators and charged back to the discharger at a certain rate per mass unit.

Many substances that contribute to B.O.D. are useful to the discharger and can be reused in the original process or sold to alternative users to negate the costs of  
10 water treatment.

We have found that the formation and subsequent coagulation of hard soaps are also capable of reducing the B.O.D. levels significantly.

The following is an example of the reduction of  
15 B.O.D. using waste effluent from the fats and oils industry.

Laboratory Procedure

A 100 mL sample of the effluent was treated with a solution of 15% calcium hydroxide ("milk of lime") to  
20 adjust the end pH to between 8.5 and 9.0.

The mixture was stirred with the aid of a magnetic stirrer.

To the effluent was added a 5% sodium oleate solution - at a volume to ensure the final concentration in solution was 0.5 g (of active sodium oleate) per litre of  
25 effluent.

The solution was allowed to stir for 5 minutes before a batch flotation test was undertaken to separate the coagulated slurry from the bulk water.

The water and initial effluent were then  
30 analysed for B.O.D. utilising a five day biological analysis procedure. The mass of sludge, sulphate concentration and suspended solids concentration for the samples were also determined and recorded.

Results

The results tabulated below indicate the capabilities of the process in lowering B.O.D. and other contaminants by utilising the process:

- 5 Sludge volumes ranged from 3.2 - 4.2 g/L. This material was found to be a useful fuel source owing to its higher relative calorific value to that of brown coal.

Element	Raw Effluent Initial Conc. (ppm)	Treated Effluent Final Conc. (ppm)
B.O.D.	4000	< 100
Suspended Solids	10000	5 - 10
Sulphate	600	< 100
Total Dissolved Solids	4200	200

Conclusion

The formation of hard soaps in the presence of substances that contribute to B.O.D. has the capability of reducing these B.O.D. levels significantly.

- 5 This lower concentration of B.O.D. and other elements allows the water to be disposed of at a lower cost than the untreated water conveying a substantial cost saving onto the end user. Alternatively the water may be of a quality in some instances to be recycled to further processing leading to savings in incoming water costs.
- 10

7. REMOVAL OF ANIONIC CONTAMINANTS

We shall now discuss the treatment of waste water to reduce the level of anionic contaminants therein.

- 15 In accordance with this aspect of the present invention there is provided a method of reducing the

concentration of an anion present in waste water which method comprises adding to the waste water a cation that is capable of forming a precipitate with the anion, adding a source of calcium or calcium plus magnesium ions to the waste water if the concentration of either or both in the waste water is insufficient to form a precipitate with a soap, adjusting the pH of the water to a level in the range from 8 to 10 and dispersing thoroughly in the waste water a fatty acid or soluble salt of a fatty acid.

The insoluble soap precipitated by the process of the invention may be removed by filtration settling or air flotation.

Contaminants removed from waste water by the process of the present invention include anions such as sulphate, phosphate, chloride, fluoride, nitrite, arsenate, arsenite, selenate, selenite, chromate and also organic anionic species such as oxalate and tartrate. The cations that may be used to precipitate these anions are typically but not exclusively ions derived from calcium, magnesium, strontium and iron. In some cases anions such as organo-sulphonates can be precipitated by using cationic organic nitrogen or organic sulphur compounds.

The fatty acid may be a saturated fatty acid comprising from 8 to 20 carbon atoms or an unsaturated fatty acid comprising from 10 to 24 carbon atoms or a mixture of the saturated and unsaturated fatty acids. Long chain saturated fatty acids may also be employed, and rosin acids or resin acids may also be used. Preferred soluble salts of the fatty acids are the alkali metal or ammonium salts. The most preferred form of fatty acid is a solution of sodium oleate.

If a fatty acid is added to the waste water it is preferably added in the form of a stable emulsion. In such a case the pH may be raised as high as 11.

One application of the invention involves the removal of sulphate ions from waste water. In this case a small excess of calcium may be added which results in the partial precipitation of these soluble calcium sulphate.

5 On standing the calcium sulphate (gypsum) slowly precipitates primarily on the container walls as a scale. However if, following the addition of the calcium the pH is raised to a level in the range between 8 and 9 and a substoichiometric amount of oleic acid as the sodium salt

10 is added, the calcium oleate formed acts as a coprecipitant, flocculant and/or adsorbent for the calcium sulphate salt and essentially all of the sulphate is efficiently removed from the solution. Excess calcium if a problem, can be removed by further additions of oleate.

15 The following examples illustrate this aspect of the process of the present invention.

Example 1

A 1 Lt aqueous solution of sodium sulphate ( $\text{SO}_4=5000$  ppm) at pH 3 was treated with 2.5 g calcium chloride di-hydrate to give a theoretical stoichiometric excess of calcium of approximately 500 ppm. With stirring

20 the soluble sulphate level in the mixture fell to 2200 ppm after 2 hrs and continued to fall slowly over several days with the formation of a gypsum (calcium sulphate) scale on

25 the container walls. After 7-8 days the soluble sulphate level was still about 800 ppm.

Example 2

The experiment was repeated, but after adding the calcium chloride di-hydrate and stirring for about 10 mins

30 the pH was raised to 8.2-8.5 with dilute sodium hydroxide and 5 mls 5% sodium oleate solution was added. The mixture was stirred for 15 mins and filtered through a coarse filter paper. The resulting soluble sulphate level was 125 ppm.



Example 3

The experiment was repeated with the calcium oleate being formed stepwise by the addition of 4 mls then a further 2 mls of 5% sodium oleate 2 mins later. After stirring for 10-15 mins to coagulate the precipitate an air flotation phase separation was carried out to remove the solids and give a solution concentration of 180 ppm sulphate. This showed that the fatty acid based precipitation is an efficient scavenge step and gives a hydrophobic product which can be readily separated by flotation.

Example 4

The experiment was repeated with the addition of 5 ppm of soluble iron, copper, zinc and manganese to the sodium sulphate solution. After removal of the calcium oleate the sulphate level was 150 ppm and the iron, copper, zinc and manganese levels were at 0.1-0.2 ppm. This showed that in the presence of the calcium sulphate the heavy metals were still efficiently removed.

Examples 5 and 6

A further experiment with a feed solution of sodium phosphate ( $\text{PO}_4=2000$  ppm) was treated with iron and calcium respectively. In the former case the iron phosphate residue was removed by adding about 600 ppm of soluble calcium, raising the pH to 8.2-8.5 with sodium carbonate or sodium hydroxide solution and then adding a sub-stoichiometric amount (30-40%) of sodium oleate with stirring to coagulate the precipitate. After filtration the phosphate level in solution was 55 ppm.

With calcium only, it was necessary to raise the pH slowly in the pH 6.5-7.5 region to allow the formation of the sparingly soluble calcium phosphate salt before the oleate addition. In this experiment the soluble phosphate level fell to 120 ppm.

Example 7

The phosphate experiment was repeated with the addition of 5 ppm of soluble copper and manganese to the feed. Again after removal of the calcium  
5 oleate/phosphate precipitate the heavy metals were present at sub 0.2 ppm levels.

8. REMOVAL OF ANIONIC AND ORGANIC CONTAMINANTS USING ORGANIC BASES

10 The removal of anions (essentially sulphate, phosphate and chloride) is normally achieved by crystallising sodium salts. This is expensive in terms of both capital and running costs. We have now developed  
15 another alternative approach using organic bases, such as nitrogen-containing fatty acid derivatives, to form insoluble or partially soluble salts which can be removed from the treated waste water.

Organic bases such as amines (primary, secondary and tertiary), amides, diamines and quaternary ammonium  
20 compounds form insoluble or partially soluble salts with sulphate anions in acidic aqueous solutions. Chloride salts formed with the organic bases tend to be more soluble but some co-removal of chloride with the sulphate precipitates is often observed.

25 Anion Precipitation Experiments

Bench scale experiments were carried out using brucine, benzidine and dodecylamine.

(a)  
30 To precipitate sulphate from dilute hydrochloric acid - only benzidine was successful, however, this is an established analytical procedure; the use of benzidine is not to be recommended, from a safety viewpoint.

- (b) Experiments on Woodlawn waste water pH 3.1,  $\text{SO}_4^{2-}$  9500ppm,  $\text{Cl}^-$  120ppm. Note: SPCC discharge limits are:

$\text{SO}_4^{2-}$  less than 250ppm

$\text{Cl}^-$  less than 250ppm

Procedure - The reagent was dispersed/dissolved in warm dilute hydrochloric acid (2% v/v) and approximately 10gms of each amine were added with stirring to 1L of waste water. The precipitate was allowed to settle and was removed by decantation and filtration. The filtrate was assayed for sulphate.

The precipitate obtained from the waste water was brown (not white as expected for a pure amine sulphate) which indicated the coprecipitation of other species with the sulphate.

Results:

Run No.	NDW 1	NDW 1	NDW 3
20 Temperature	40°C	25°C	22°C
Reaction Time	10 mins	10 mins	30 mins

$\text{SO}_4^{2-}$  levels in ppm

25 Benzidine	120	50	30
Brucine	300	200	100
Dodecylamine	350	200	100

After filtration the precipitate was treated with  $\text{Na}_2\text{CO}_3/\text{NaOH}$  at pH 10-11 to recover the amine and to solubilise the anions. Recoveries of 85-90% were obtained.

Further Experiments on Sulphate Removal

Test solutions were prepared from mixtures of Sulphuric Acid, Sodium Sulphate and Sodium Hydroxide to

give a 3,000 ppm and 10,000 ppm sulphate solution at pH values of 3, 5, 7 and 8.

A temperature of 30°C was maintained during the experiments.

5           The surfactants used were -

Sodium lauryl sulphate (SLS)

Alkyl benzene sulphonate (ABS)

Ligoin sulphonate (LS)

10

Dodecylamine (in about 2% solution) was dispersed in 1% (v/v) HCl and added in slight excess to the sulphate test solutions. These were then stirred for 30 minutes. The dispersions were treated with 0.2 ml 0.1% surfactant and stirred for a further 2 minutes.

15

Solid/liquid separation was achieved using an 0.45 micron micro filtration assembly.

#### Results

Feed-3,000 ppm Sulphate Solution

20

Filtrate SO<sub>4</sub> content (ppm)

	<u>Surfactant</u>	<u>SLS</u>	<u>ABS</u>	<u>LS</u>
	pH of feed solution			
	3	550	300	160
25	5	350	200	200
	7	150	200	150
	8	250	450	450

30

Feed-10,000 ppm Sulphate Solution

Filtrate SO<sub>4</sub> content (ppm)

	<u>Surfactant</u>	<u>SLS</u>	<u>ABS</u>	<u>LS</u>
5	pH of feed solution			
	3	600	250	150
	5	300	200	200
	7	100	300	130
	8	250	500	400

10

The maximum permitted discharge levels for sulphate is 250 ppm. The results obtained indicate that low sulphate levels can be achieved in aqueous effluents (below 250 ppm).

15 Further Experiments with Organic Bases

Further tests with industrial waste waters have demonstrated that organic bases are capable of removing both anions and organic materials that contribute to B.O.D. and/or C.O.D.

20 Experimental

A sample of waste water from a wool scouring mill was used for the experimental work.

A 1L waste water sample of pH 8-9 was adjusted to pH 3.5 with 18N H<sub>2</sub>SO<sub>4</sub>.

25 A total of 0.5g/L of a commercial primary fatty amine was then added to this sample and stirred for a period of 10 minutes.

The resulting precipitate was removed from the bulk sample using a conventional flotation technique. The feed, 30 and the treated sample were then analysed for B.O.D., suspended solids, sulphate and nitrogen. The results are indicated in the table below.

	FEED EFFLUENT QUALITY (PPM)	TREATED EFFLUENT QUALITY (PPM)
WOOL SCOURING SAMPLE	B.O.D. 7000 S.S. 5000 SO <sub>4</sub> 400 N 120	B.O.D. 150 S.S. 10 SO <sub>4</sub> <100 N 30

The solid sludge remaining after flotation was dewatered to yield a solid of 35% moisture. This is significantly lower in moisture than many conventional  
5 sludges formed in the treatment of waste water. The results clearly indicate that organic bases are effective in the removal of both anionic and organic contaminants in concert.

10 9. REAGENT RECYCLING

A study of reagent recycling was conducted to determine the efficiency of the recycling of oleic acid from the precipitated salts through the acid compounds and  
back to the soluble reagent.

15 The recycling of the reagent was deemed necessary to improve the economics of the reagent consumption compared to a one off application basis. The recycling also allowed the contaminant to be concentrated in a form so that it could be reused in other processes  
20 where possible.

Experimental

A weighed 50 gram fraction of a Ca(Mg) oleate precipitate was dispersed in 0.5M H<sub>2</sub>SO<sub>4</sub> in a test tube. With stirring the salt is decomposed resulting in a  
25 solution of MgSO<sub>4</sub>, a precipitate of CaSO<sub>4</sub>, and an oleic acid oil layer which rose to the surface. The separation of the

phases were assisted by raising the temperature to 40 - 50°C followed by centrifuging at 1000 rpm for 2 - 3 minutes.

5 The oleic acid formed was carefully removed by pipette, along with a small amount of the oleic/CaSO<sub>4</sub> emulsion present. This ensured maximum recovery of the oleic acid component. The mixture was then treated with 10% NaOH to recover the oleic acid as the soluble sodium oleate salt.

10 The sodium oleate was then added to a Woodlawn acid mine water sample and the resulting precipitate filtered, dried and weighed. The reconstitution of the sodium oleate was repeated. The procedure was repeated four times consecutively prior to storage. The experiment  
15 was repeated one week later on the stored precipitate to determine any ageing effects of the precipitate may have on recycling.

The results from the testwork are indicated in the chart below:

Number of recycles	Weight (g)	Yield(%)
1 recycle	46.1	91.9
2 recycles	39.2	85.0
3 recycles	34.9	89.1
4 recycles	30.7	88.0
After 1 week then recycle	27.0	87.9
Average fatty acid recovery		88.4

Conclusions

The results indicate that the reagent recycling concept is capable of re-using a major proportion of the reagent on a continual basis. This assists in minimising the costs per unit volume of the treatment process.

In the particular embodiment of the invention illustrated in Figure 4.1, contaminated water is fed to a neutralisation vessel 4 together with lime slurry fed via line 2 from source 3. Slurry may leave the neutralisation vessel 4 via line 5 to an optional filter 6 from which solids are removed via line 7. Overflow from the neutralisation vessel 4 passes via line 8 to a high shear reagent mixing vessel line 9, which also receives water from the filter 6 via line 10 and recycled sodium oleate 11 via line 12. From the mixing zone 9 the mixture passes through reaction tanks 13 and 14 to a flotation cell 15 from which water is removed via line 16 while solids are removed via line 17 to a filter 18. Water from the filter 18 is removed via line 19 and combined with the water in line 16, to constitute the treated water for discharge via line 20. Solids for recycle leave the filter 18 via line 21 for acidification and neutralisation in regeneration vessel 22. Regenerated sodium oleate is collected in vessel 11 for recycle via line 12.

In a further embodiment of the invention illustrated in Figure 5.1, acid is added to the waste water before the neutralisation step. In this embodiment effluent entering via line 1 is mixed in vessel 2 with an acid, suitably sulphuric acid, added via line 3. Overflow from vessel 2 passes via line 4 to neutralisation vessel 5 to which a lime slurry, suitably 15% milk of lime, is added via line 6. Overflow from the neutralisation vessel 5 passes via line 7 to a high shear reagent mixing vessel 9, which also receives the reagent, for example sodium oleate,



via line 8. From the mixing vessel 9 the reaction product passes via line 10 to a flotation cell 11 for solid/liquid separation, water for disposal or recycle being removed via line 13. Air for the flotation process is supplied via line 12 and solids in the form of concentrated sludge are removed via line 14 for subsequent separation and regeneration of reagent in stages not shown.

It will be clearly understood that the invention in its general aspects is not limited to the specific details referred to hereinabove.

CLAIMS:

1. A method of treating waste water to remove  
contaminants therefrom, which comprises forming a  
5 precipitate of at least one insoluble soap in situ and  
removing the precipitate, said precipitate containing at  
least a portion of at least one contaminant.
2. A method according to claim 1, in which the  
contaminants include hard cations such as calcium and/or  
10 magnesium, and the precipitate is formed by adding one or  
more fatty acids or fatty acid salts to the waste water.
3. A method according to claim 1 in which the waste  
water contains insufficient hard cations to form an  
effective precipitate and a source of calcium and/or  
15 magnesium ions is added to the waste water as well as one  
or more fatty acids or fatty acid salts in order to form  
the precipitate.
4. A method according to claim 1, which comprises  
adding to the waste water at least one fatty acid or fatty  
20 acid salt selected from the group consisting of straight or  
branched chain, saturated or at least mono-unsaturated  
fatty acids having from 8 to 24 carbon atoms, and the  
alkali metal salts thereof.
5. A method according to claim 4 which comprises  
25 adding sodium oleate to the waste water.
6. A method according to claim 2, in which the waste  
water contains contaminants other than calcium and/or  
magnesium and at least a portion of said other contaminants  
is removed with the precipitate.
- 30 7. A method according to claim 6, in which the  
contaminants in the waste water comprise at least one of  
lead, copper, iron, manganese, cadmium aluminium and  
organic contaminants.

8. A method according to claim 7 in which the organic contaminants comprise at least one of benzene, aniline, cyclohexane, acrylonitrile, kerosene, petrol and contaminants contributing to B.O.D. and/or C.O.D.
- 5 9. A method according to claim 1 in which the waste water contains anionic contaminants, which comprises adding to the waste water a cation that is capable of forming a precipitate with the anion, adding a source of calcium or calcium plus magnesium ions to the waste water if the  
10 concentration of the said calcium or calcium plus magnesium ions in the waste water is insufficient to form a precipitate with a soap, adjusting the pH of the water to a level in the range from 8 to 10 and dispersing thoroughly therein a fatty acid or soluble salt of a fatty acid.
- 15 10. A method according to claim 9 in which the anionic contaminants include at least one of sulphate, phosphate, chloride, fluoride, nitrite, arsenate, arsenite, selenate, selenite, chromate, and organic anionic species such as oxalate and tartrate, and the cations used to precipitate  
20 these anions are at least one of calcium, magnesium, strontium and iron.
- 25 11. A method according to claim 10 in which sulphate ions are precipitated from waste water by adding a small excess of calcium ions, raising the pH to a level between 8 and 9, and adding sodium oleate in a sub-stoichiometric amount, whereby substantially all of the sulphate is precipitated together with the calcium oleate.
- 30 12. A method of treating waste water to remove contaminants therefrom, which comprises feeding waste water to a vessel in which the pH is adjusted by addition of acid and/or alkali to a value suitable for the precipitation of an insoluble soap, adding a reagent which comprises at least one of fatty acid, fatty acid salt, fatty acid amine and fatty acid salt, to the pH adjusted water to form a

precipitate and separating the precipitate; treating the separated precipitate by acidification and saponification to regenerate the reagent, and recycling regenerated reagent to the precipitation step.

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## AMENDED CLAIMS

[received by the International Bureau on 13 July 1993 (13.07.93); original claims 1,3,6 and 12 amended; other claims unchanged (3 pages)]

1. A method of treating waste water to remove contaminants therefrom, which comprises adding a reagent  
5 which comprises one or more fatty acids, fatty acid salts, fatty acid amines and/or fatty acid amine salts to the waste water to form a precipitate of at least one insoluble soap in situ and removing the precipitate, said precipitate containing at least a portion of at least one contaminant.
- 10 2. A method according to claim 1, in which the contaminants include hard cations such as calcium and/or magnesium, and the precipitate is formed by adding one or more fatty acids or fatty acid salts to the waste water.
- 15 3. A method according to claim 1 in which the waste water contains insufficient hard cations to form an effective precipitate and a source of calcium and/or magnesium ions is added to the waste water as well as the said reagent in order to form the precipitate.
- 20 4. A method according to claim 1, which comprises adding to the waste water at least one fatty acid or fatty acid salt selected from the group consisting of straight or branched chain, saturated or at least mono-unsaturated fatty acids having from 8 to 24 carbon atoms, and the alkali metal salts thereof.
- 25 5. A method according to claim 4 which comprises adding sodium oleate to the waste water.
6. A method according to claim 2 or claim 3, in which the waste water contains contaminants other than calcium and/or magnesium and at least a portion of said  
30 other contaminants is removed with the precipitate.
7. A method according to claim 6, in which the contaminants in the waste water comprise at least one of lead, copper, iron, manganese, cadmium aluminium and organic contaminants.

8. A method according to claim 7 in which the organic contaminants comprise at least one of benzene, aniline, cyclohexane, acrylonitrile, kerosene, petrol and contaminants contributing to B.O.D. and/or C.O.D.
- 5 9. A method according to claim 1 in which the waste water contains anionic contaminants, which comprises adding to the waste water a cation that is capable of forming a precipitate with the anion, adding a source of calcium or calcium plus magnesium ions to the waste water if the
- 10 concentration of the said calcium or calcium plus magnesium ions in the waste water is insufficient to form a precipitate with a soap, adjusting the pH of the water to a level in the range from 8 to 10 and dispersing thoroughly therein a fatty acid or soluble salt of a fatty acid.
- 15 10. A method according to claim 9 in which the anionic contaminants include at least one of sulphate, phosphate, chloride, fluoride, nitrite, arsenate, arsenite, selenate, selenite, chromate, and organic anionic species such as oxalate and tartrate, and the cations used to
- 20 precipitate these anions are at least one of calcium, magnesium, strontium and iron.
11. A method according to claim 10 in which sulphate ions are precipitated from waste water by adding a small excess of calcium ions, raising the pH to a level between 8
- 25 and 9, and adding sodium oleate in a sub-stoichiometric amount, whereby substantially all of the sulphate is precipitated together with the calcium oleate.
12. A method of treating waste water to remove contaminants therefrom, which comprises feeding waste water
- 30 to a vessel in which the pH is adjusted by addition of acid and/or alkali to a value suitable for the precipitation of an insoluble soap, adding a reagent which comprises at least one of fatty acid, fatty acid salt, fatty acid amine and fatty acid amine salt, to the pH adjusted water to form

a precipitate and separating the precipitate; treating the separated precipitate by acidification and saponification to regenerate the reagent, and recycling regenerated reagent to the precipitation step.

5

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## STATEMENT UNDER ARTICLE 19

Claims 1, 3, 6 and 12 of the international application are amended concurrently herewith.

The amendments clarify the claims and distinguish the invention more clearly from the art cited in the International Search Report dated 14 May 1993.

Claim 1 now specifies that the precipitate is formed by adding a reagent (as defined) to the waste water. The reagent is defined in conformity with claim 12.

Claim 3 now refers to "the said reagent", and claim 6 is appended to claim 3 as well as claim 2.

In claim 12 in the last line of page 41, the word "amine" was omitted after "acid" and is now inserted.

The cited references JP 52-012,763 and JP 52-012,764 which are almost identical in content, relate to treatment of waste water containing sodium salts of fatty acids or foaming substances with a high BOD load, by adding calcium or magnesium ions and removing the resulting precipitate before carrying out an activated sludge process. These references neither disclose nor suggest the process of the present invention as defined in amended claim 1.

SU 1,293,116 relates to flotation. Heavy metals are removed from waste water by using  $C_8$ - $C_{18}$  fatty acids or abietic acid dissolved in paraffin. This is totally different from the present invention.

In SU 1,291,549 a petroleum mazout fraction is added to the waste water to assist in increased metal removal by subsequent carbon adsorbent treatment. This implies a two-stage treatment, in the first stage of which totally different chemicals are used.

SU 1,627,522 and JP 60-197294 were cited in category "A" only and require no comment.



1/20

# Sedimentation Testwork

## Flowsheet Outline

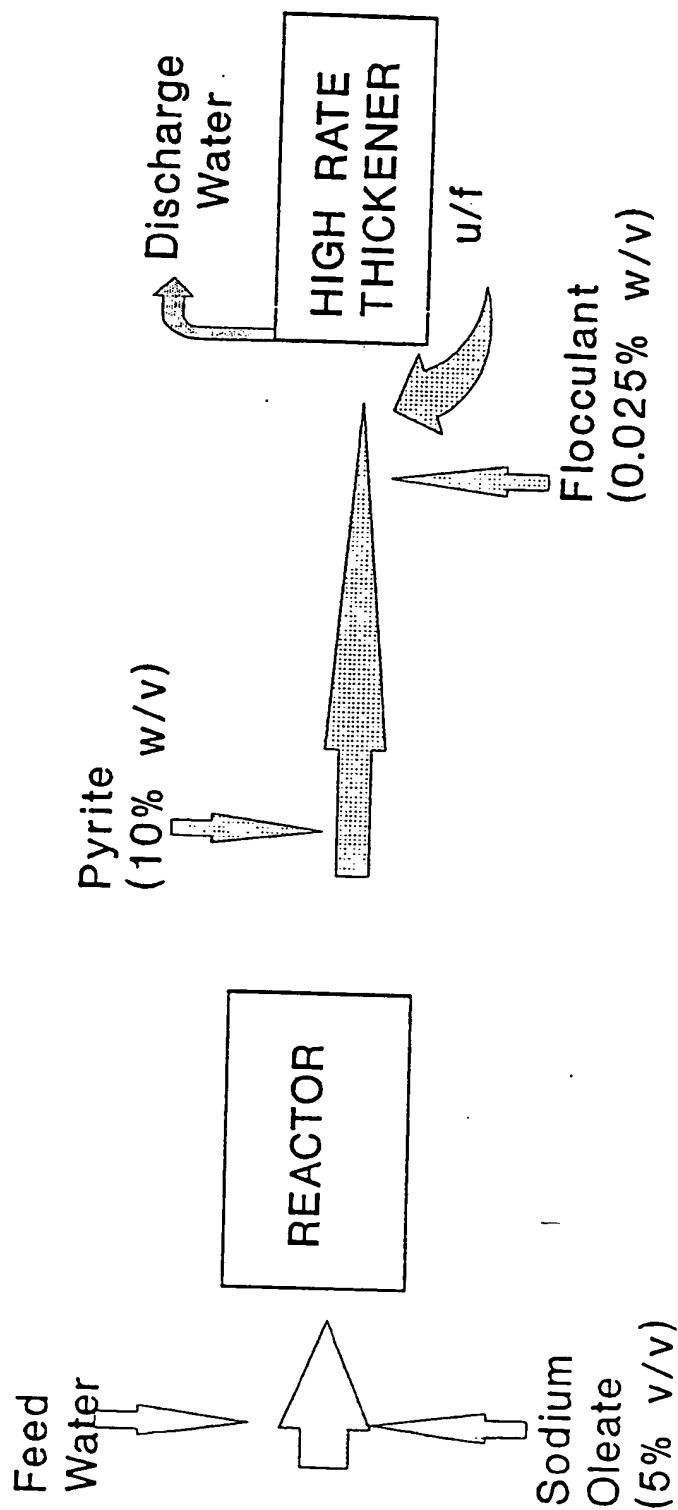


Figure 1.1

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# Water Purification Sedimentation Results

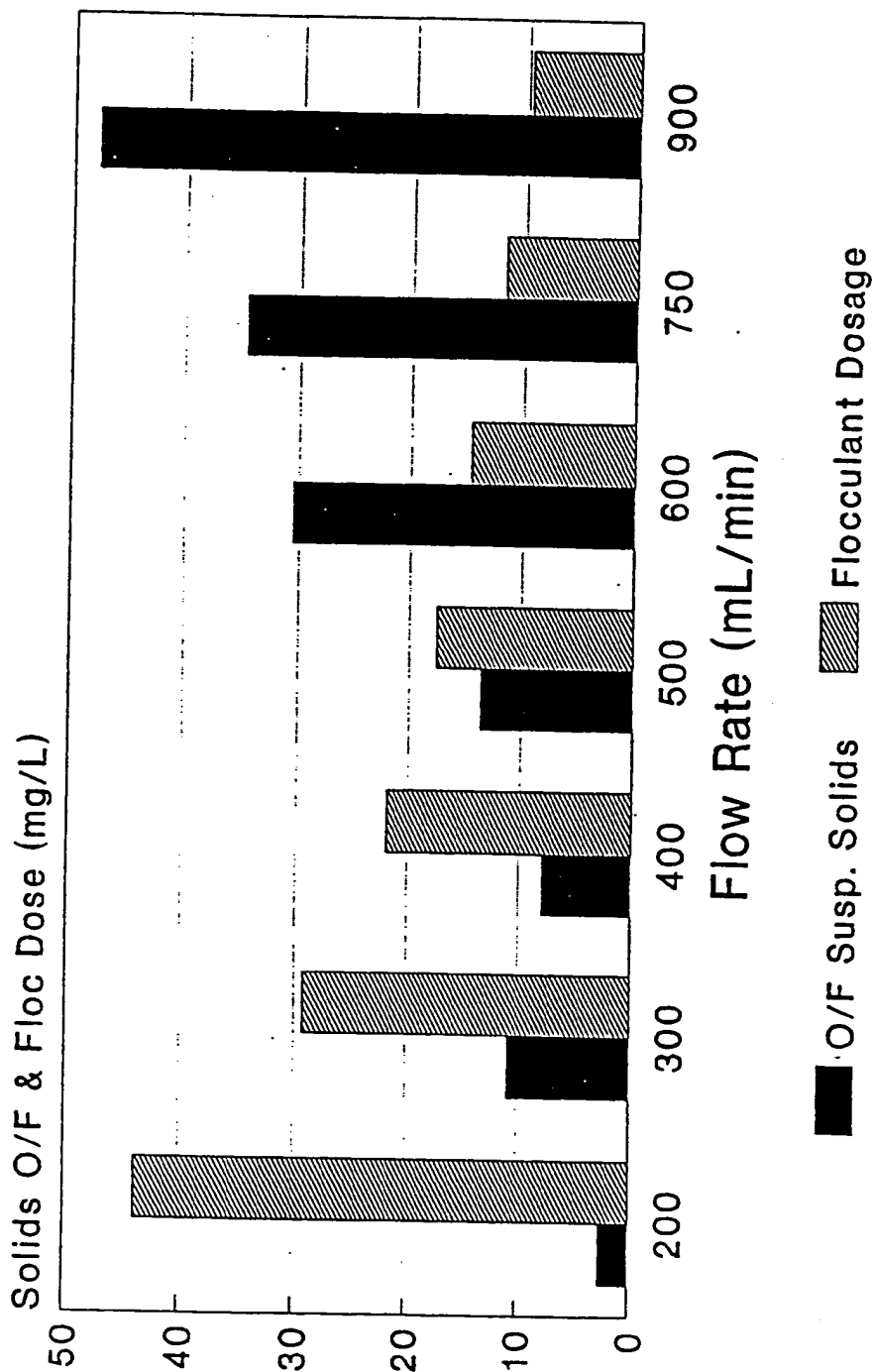


Figure 1.2

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# Water Purification Sedimentation Results

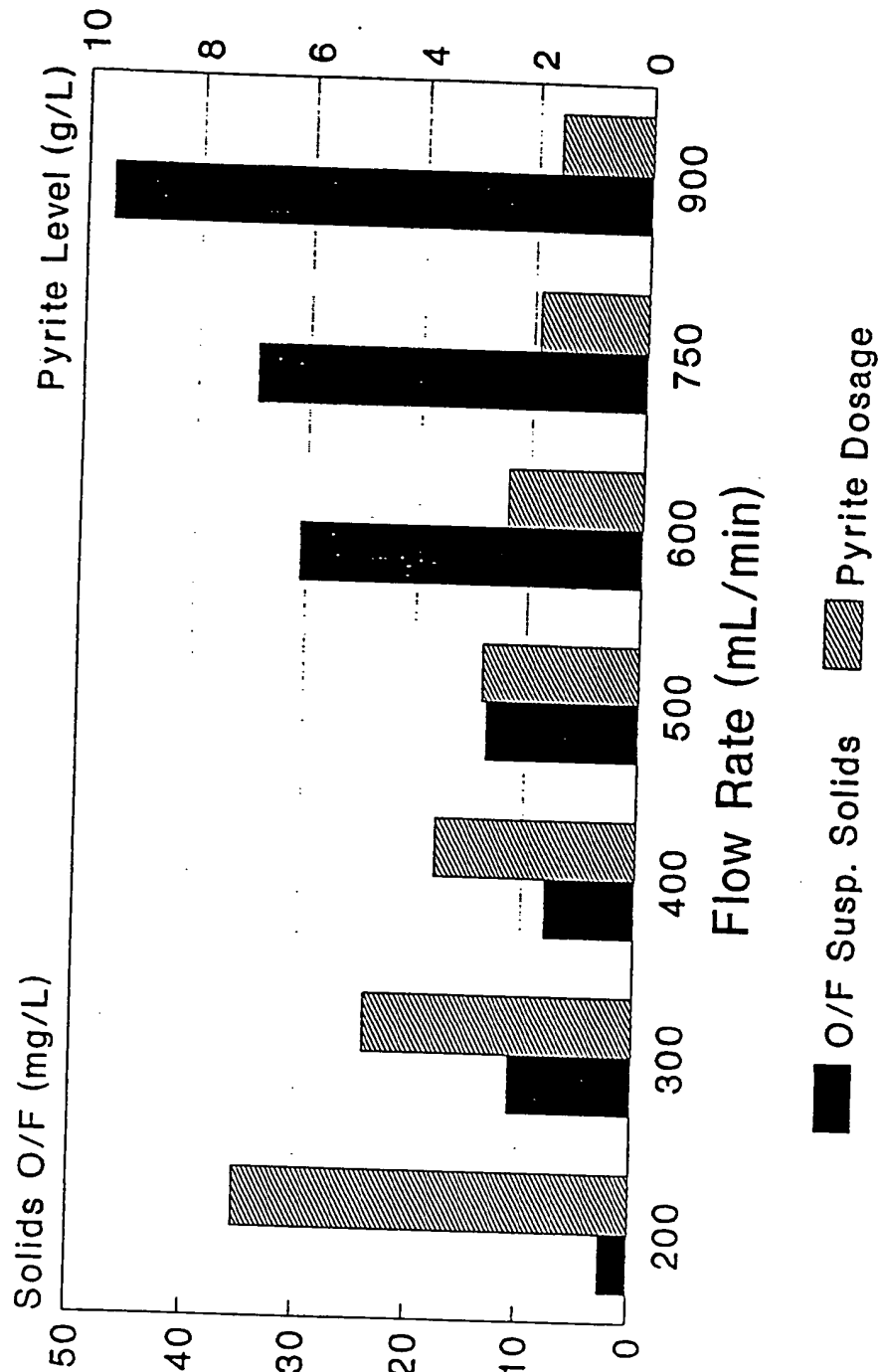


Figure 1.3

# Water Purification

## Reaction Kinetics - 0.06 g/L reagent

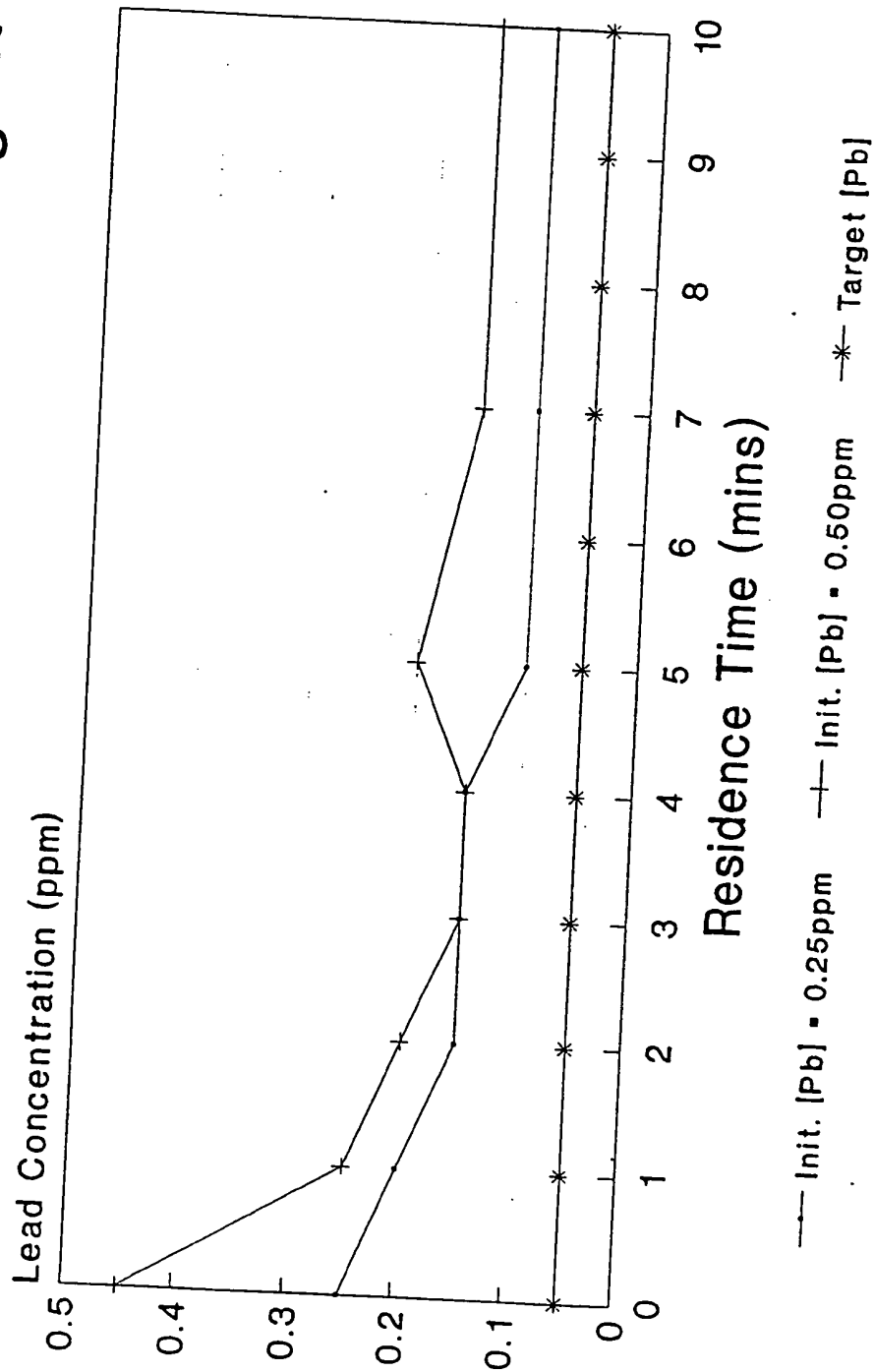


Figure 2.1

# Water Purification

## Reaction Kinetics - 0.12 g/L reagent

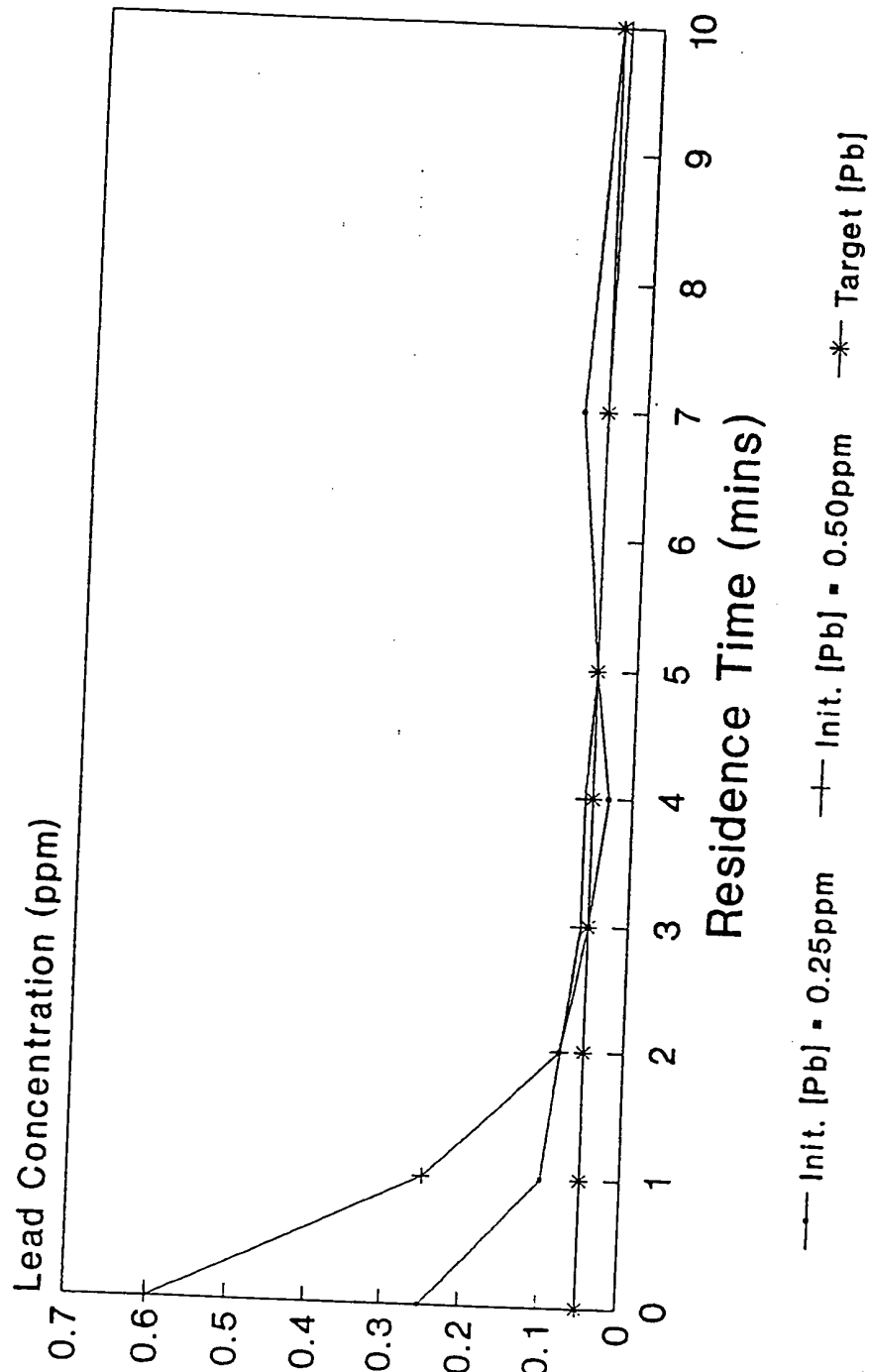


Figure 2.2

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# Water Purification

## Reaction Kinetics - 0.24 g/L reagent

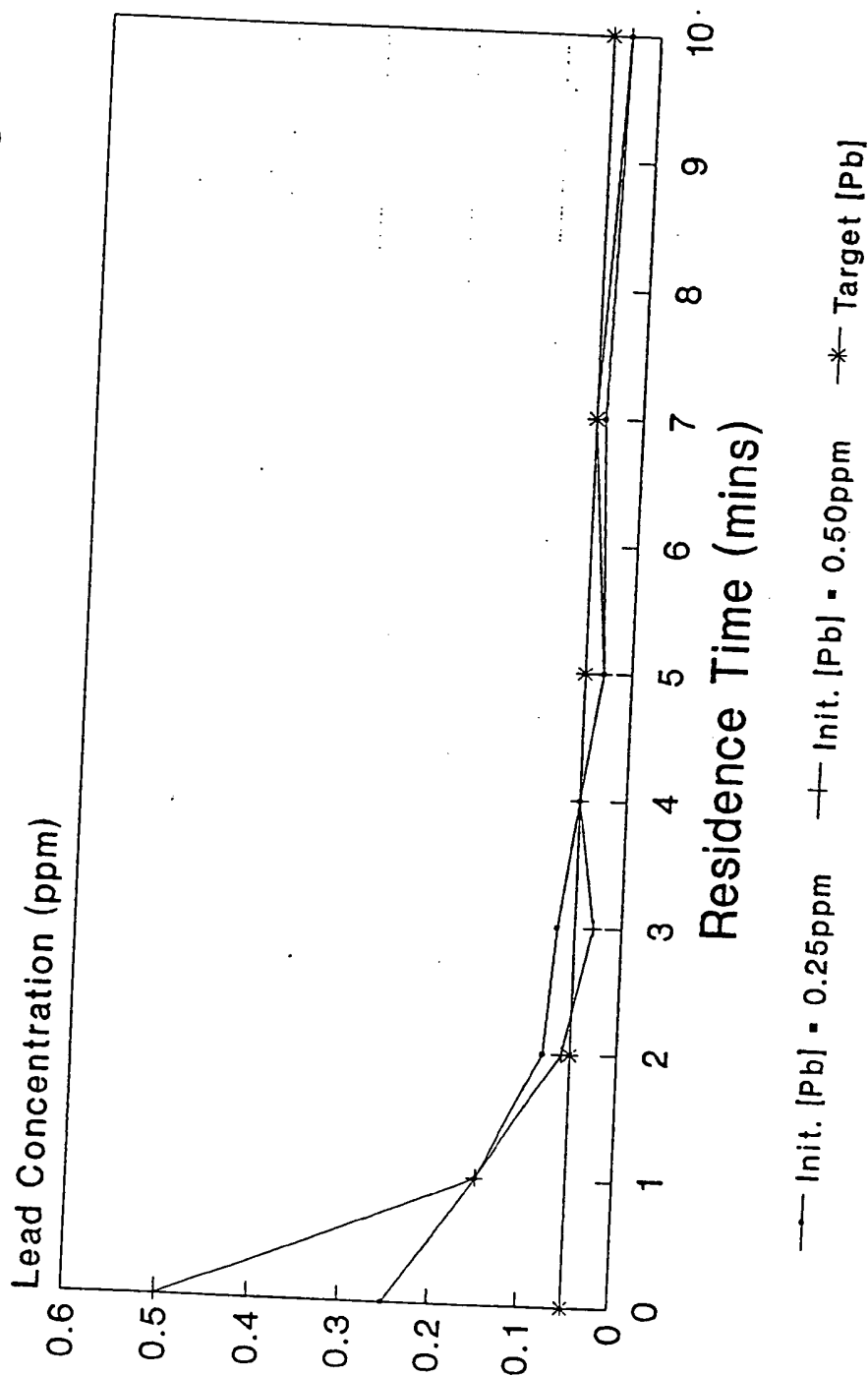


Figure 2.3

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# Water Purification

## Reaction Kinetics - 0.36 g/L reagent

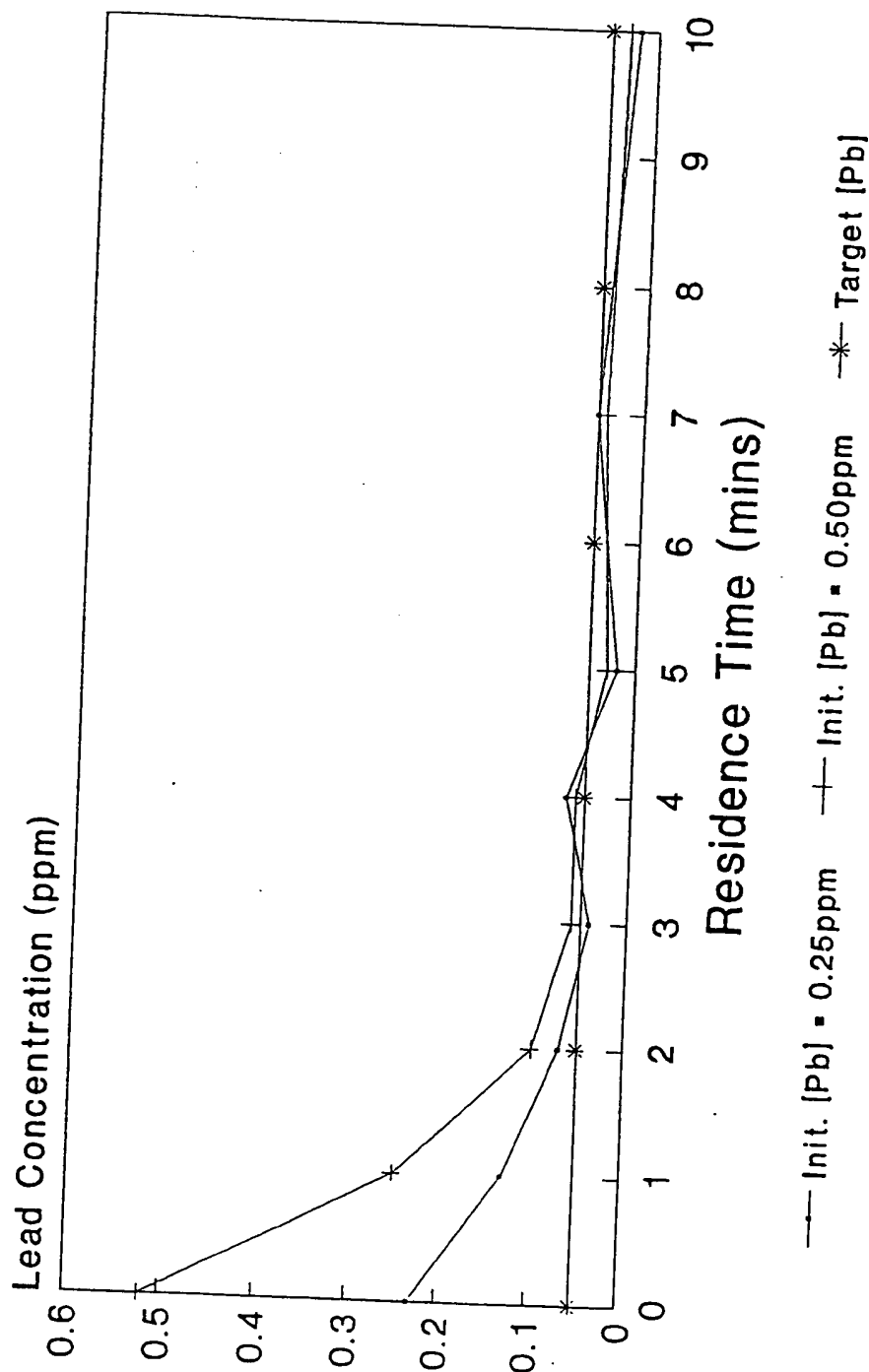


Figure 2.4

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# Water Purification

## Reaction Kinetics - 0.50 g/L reagent

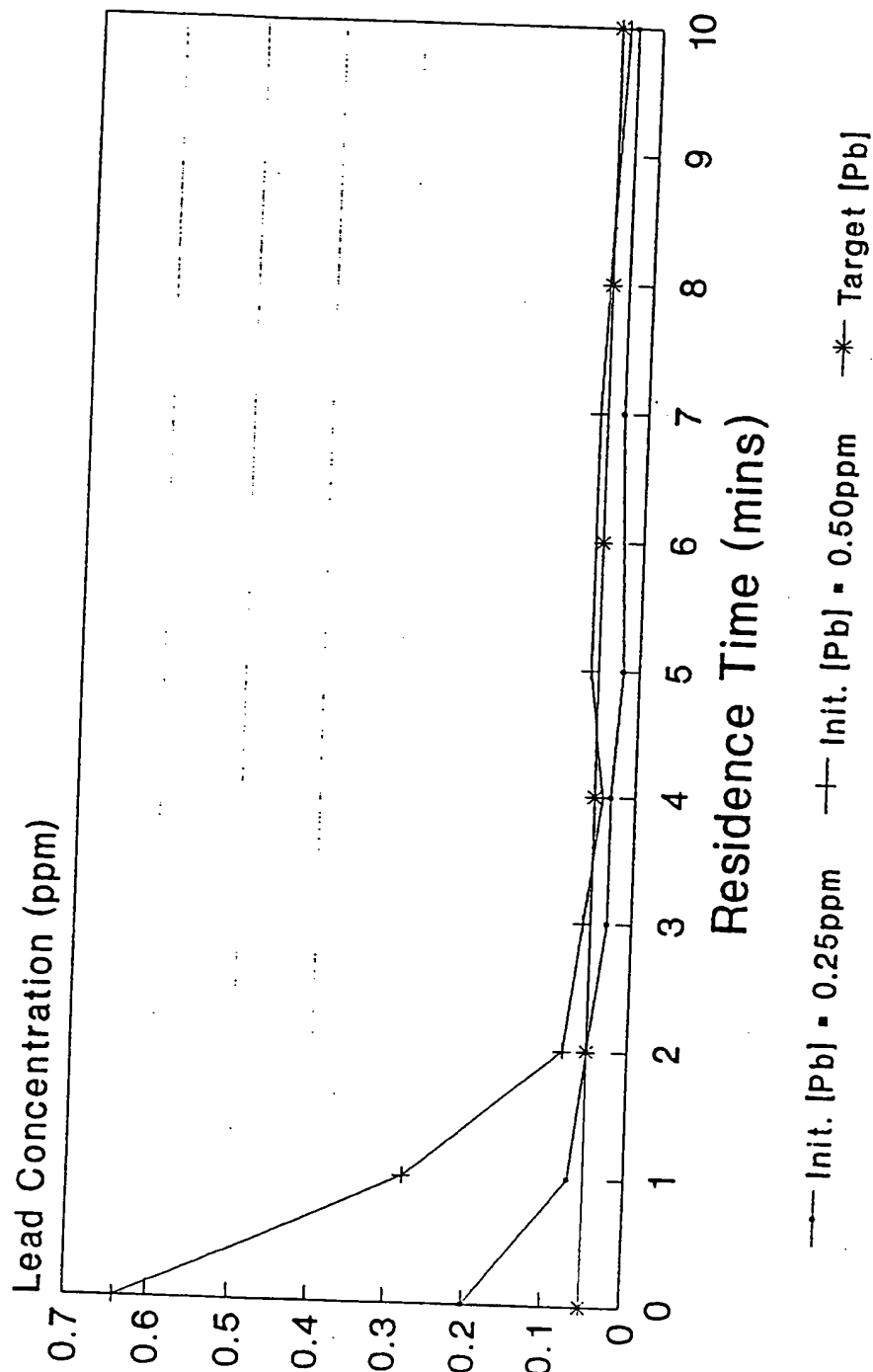


Figure 2.5



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# Water Purification

## Reaction Kinetics - 1.00 g/L reagent

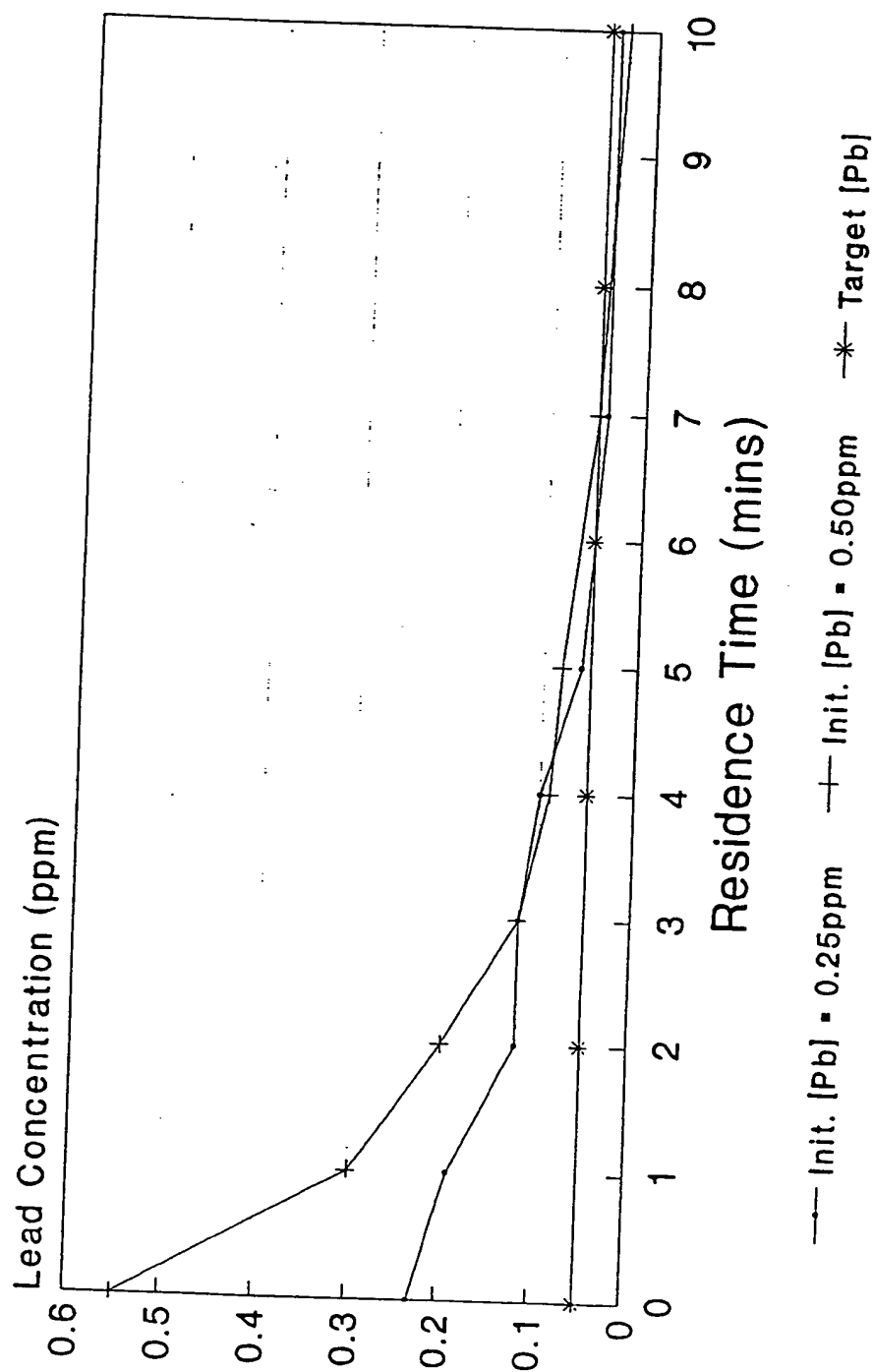


Figure 2.6

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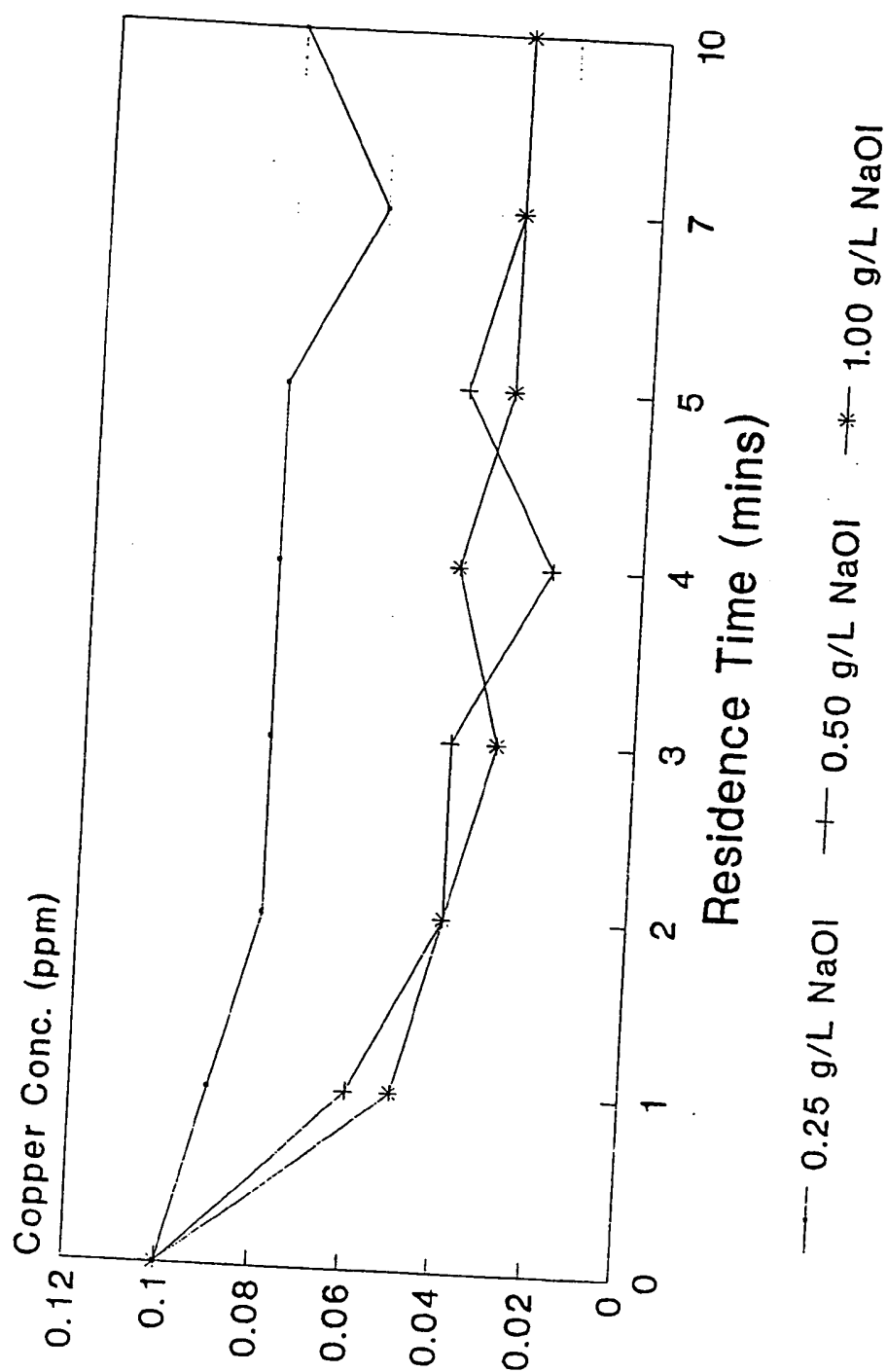


Figure 3.1

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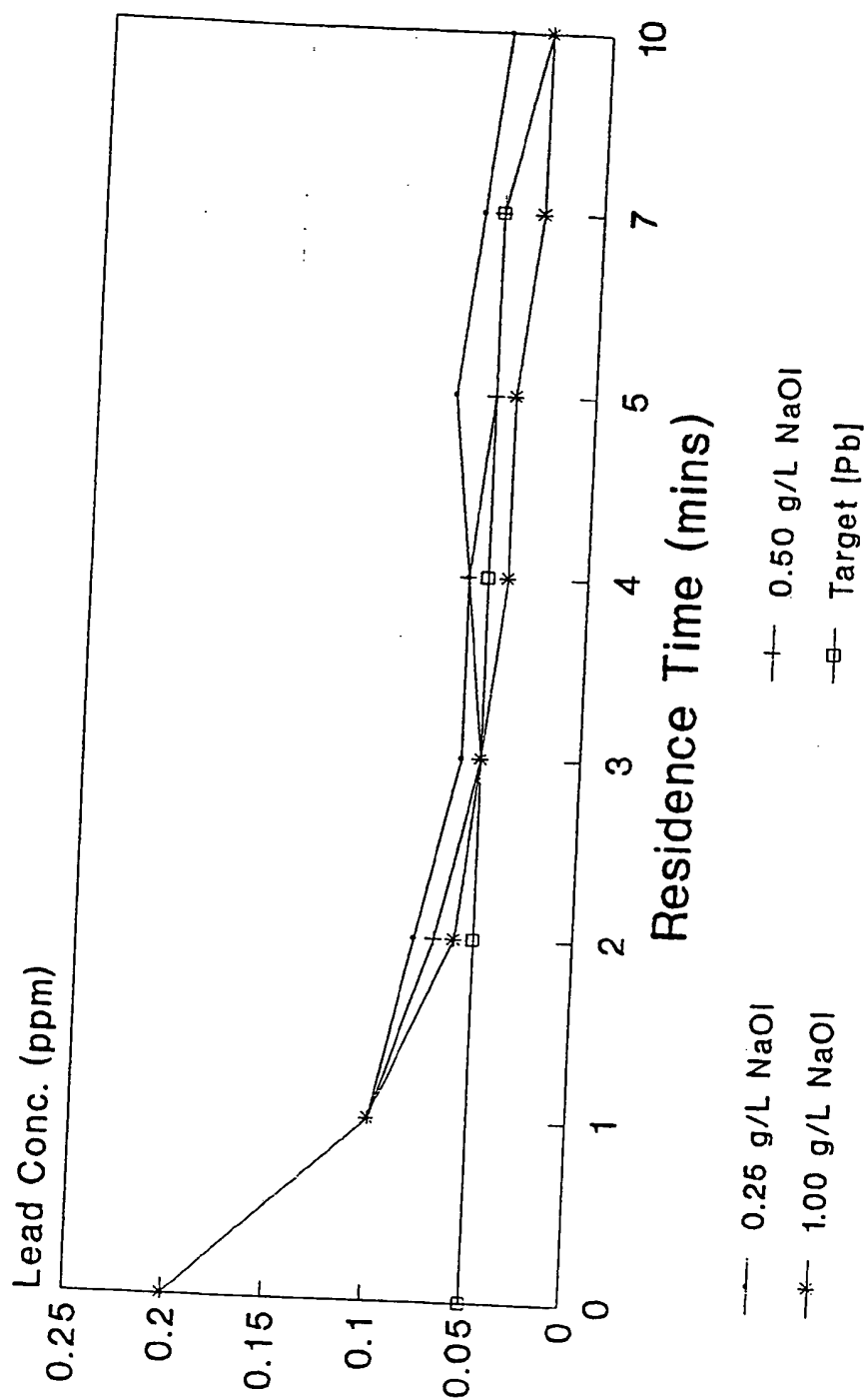


Figure 3.2

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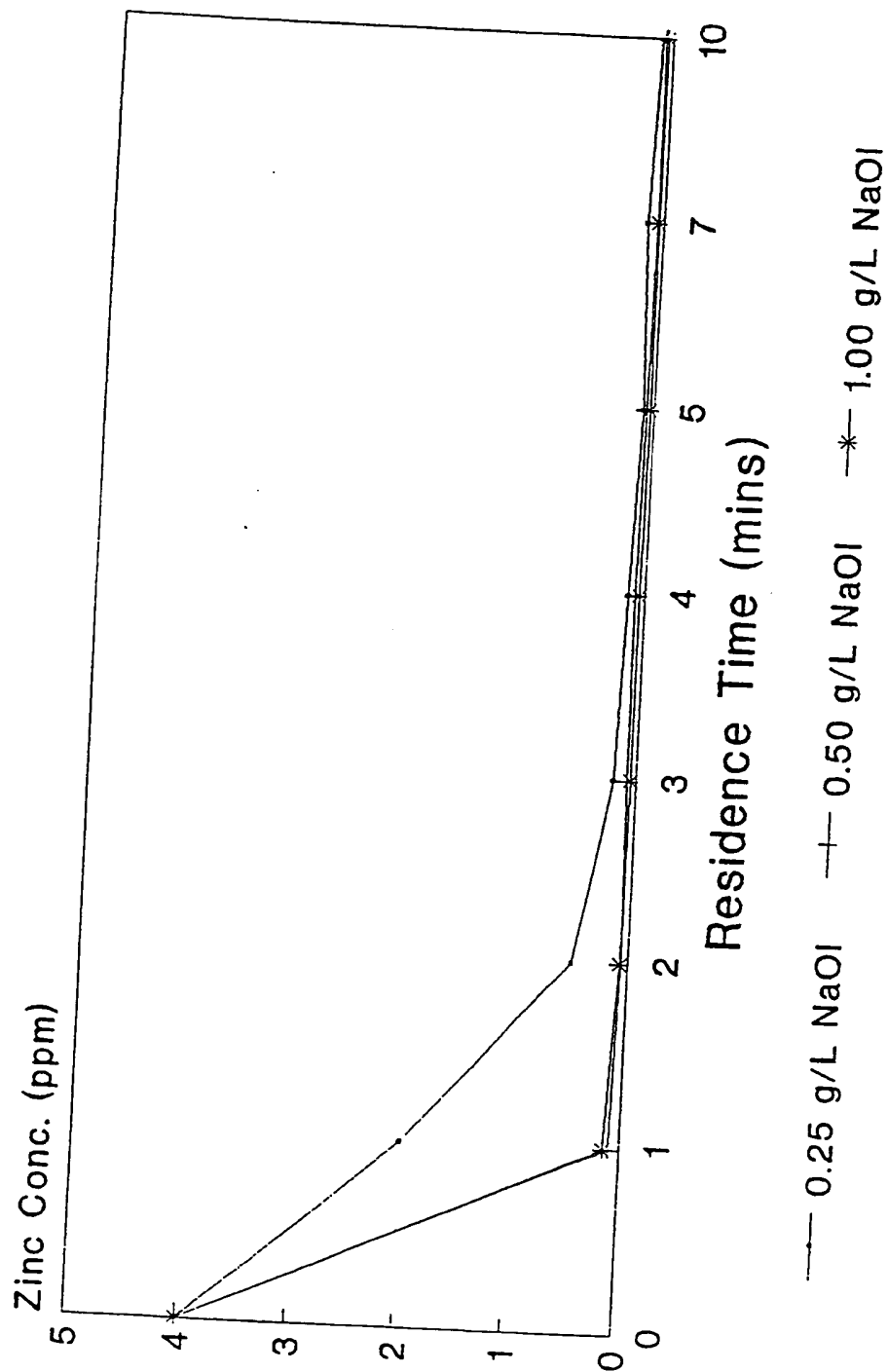


Figure 3.3

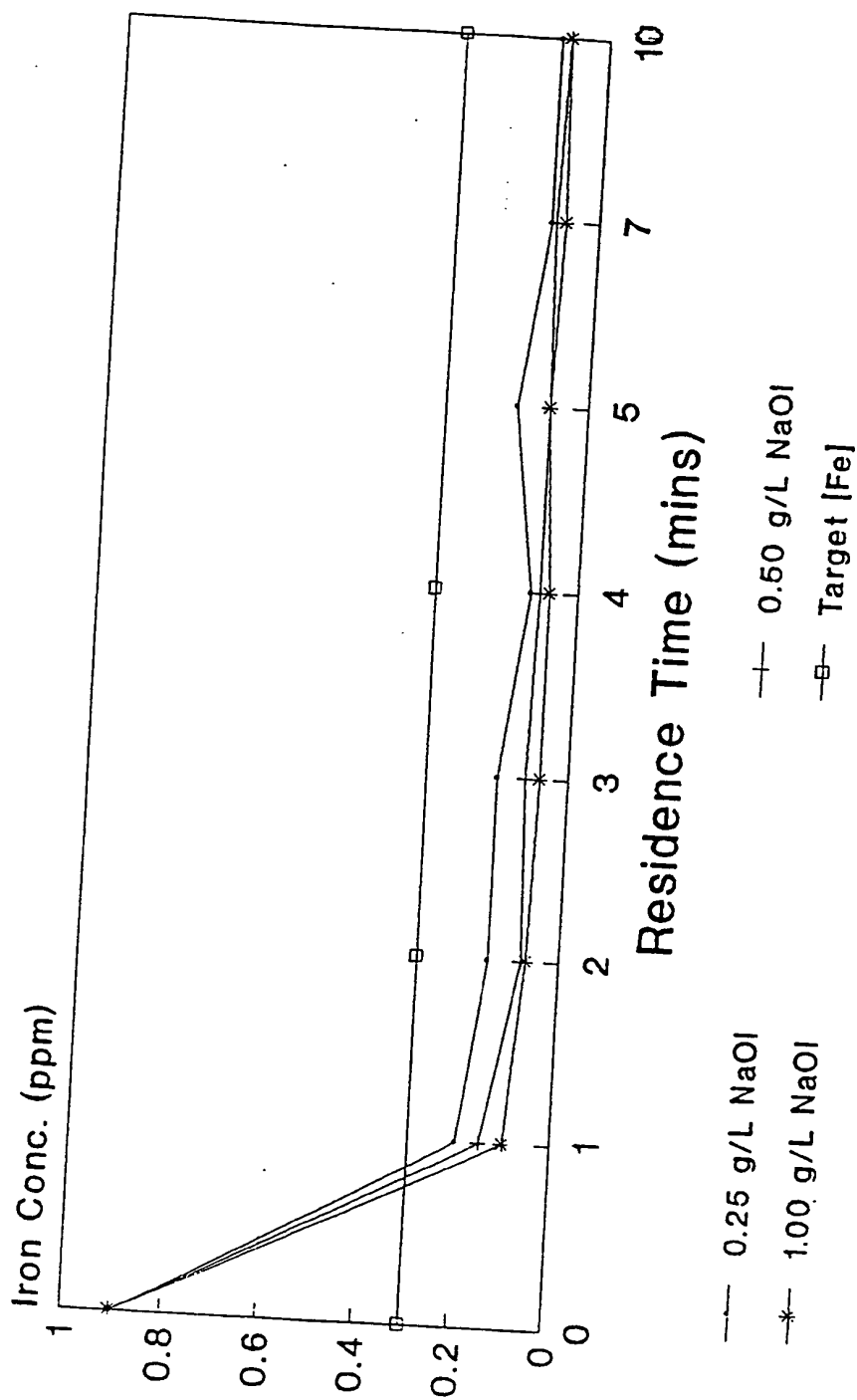


Figure 3.4

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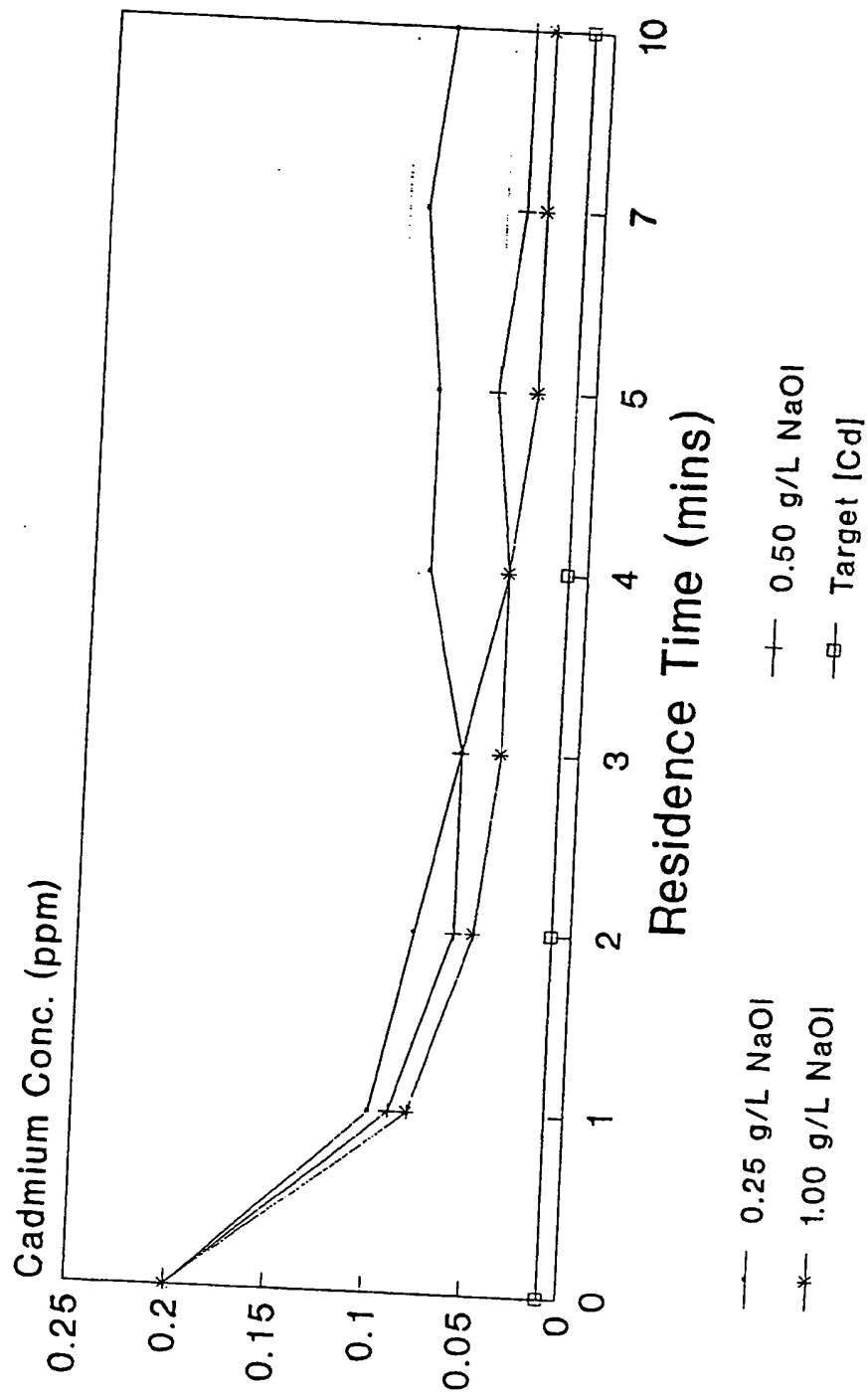


Figure 3.5

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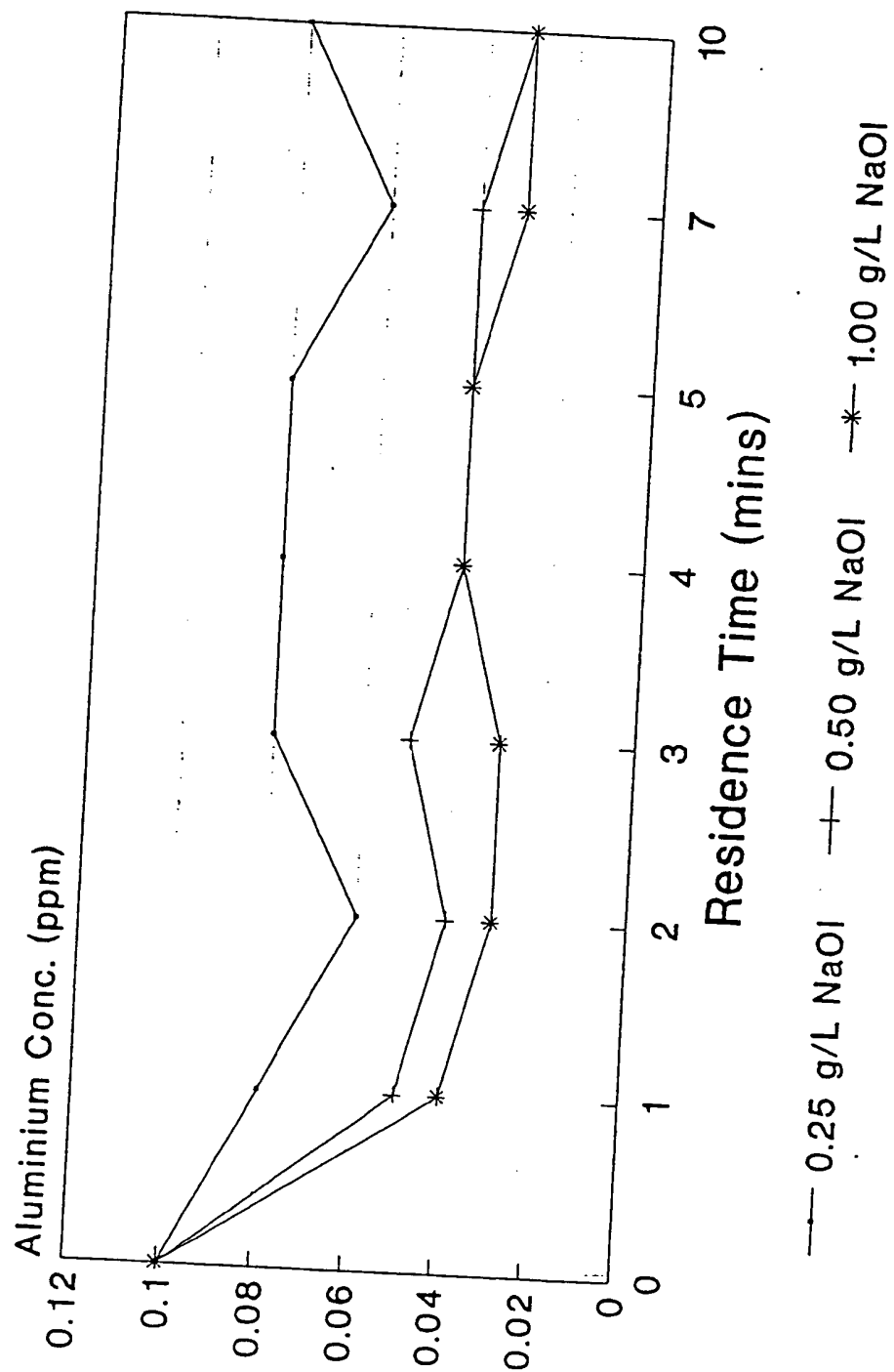


Figure 3.6

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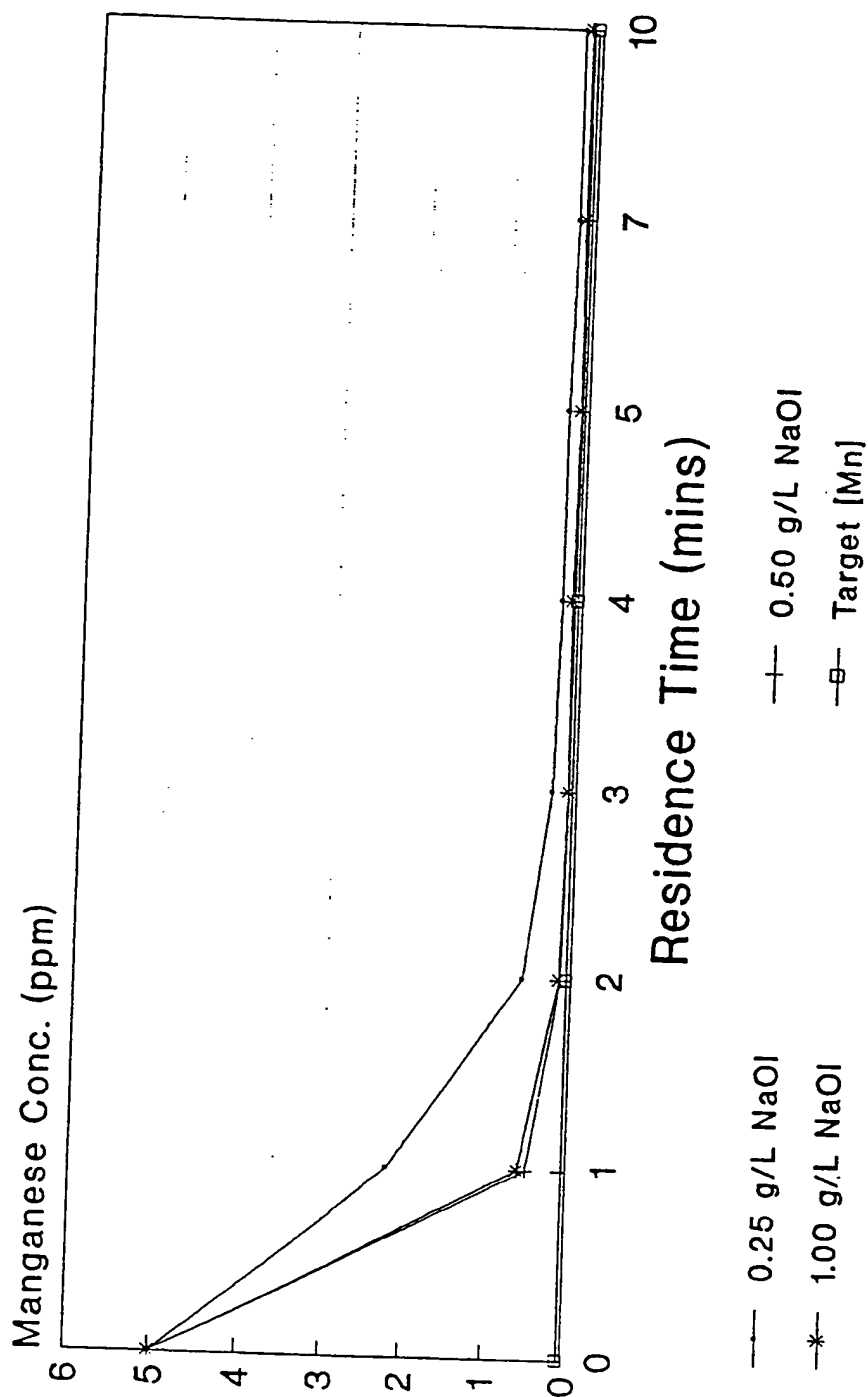


Figure 3.7



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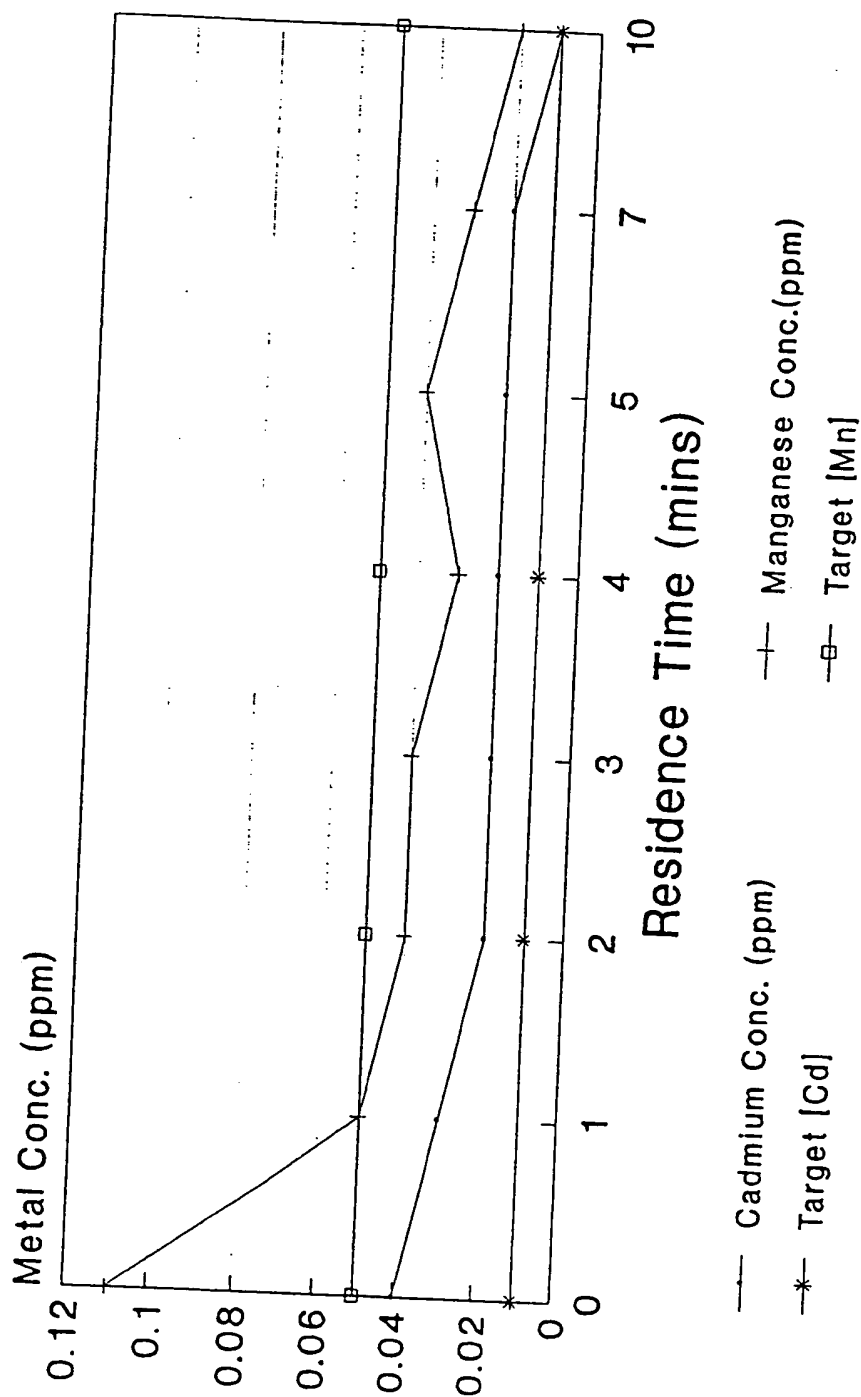


Figure 3.8

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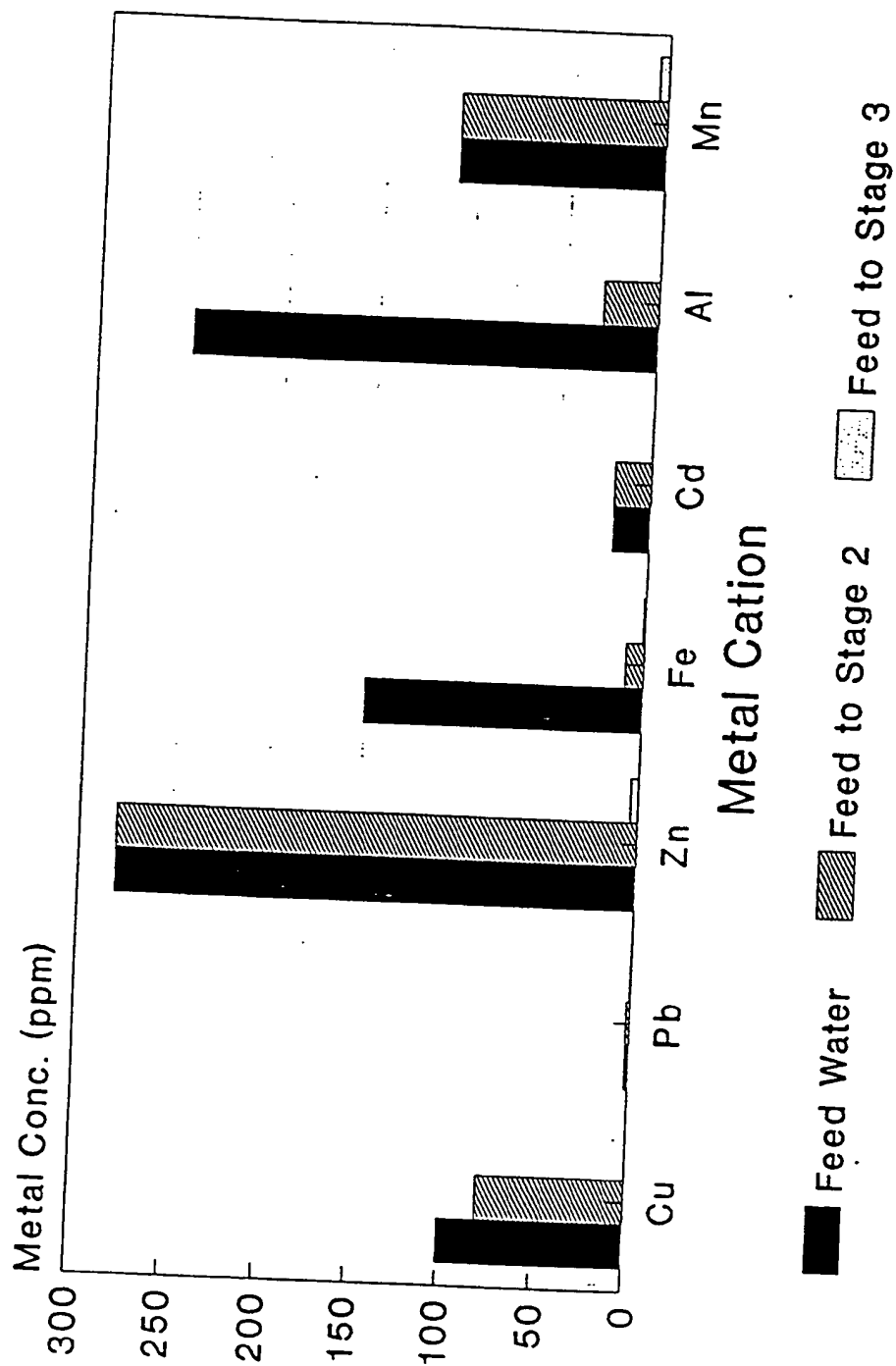
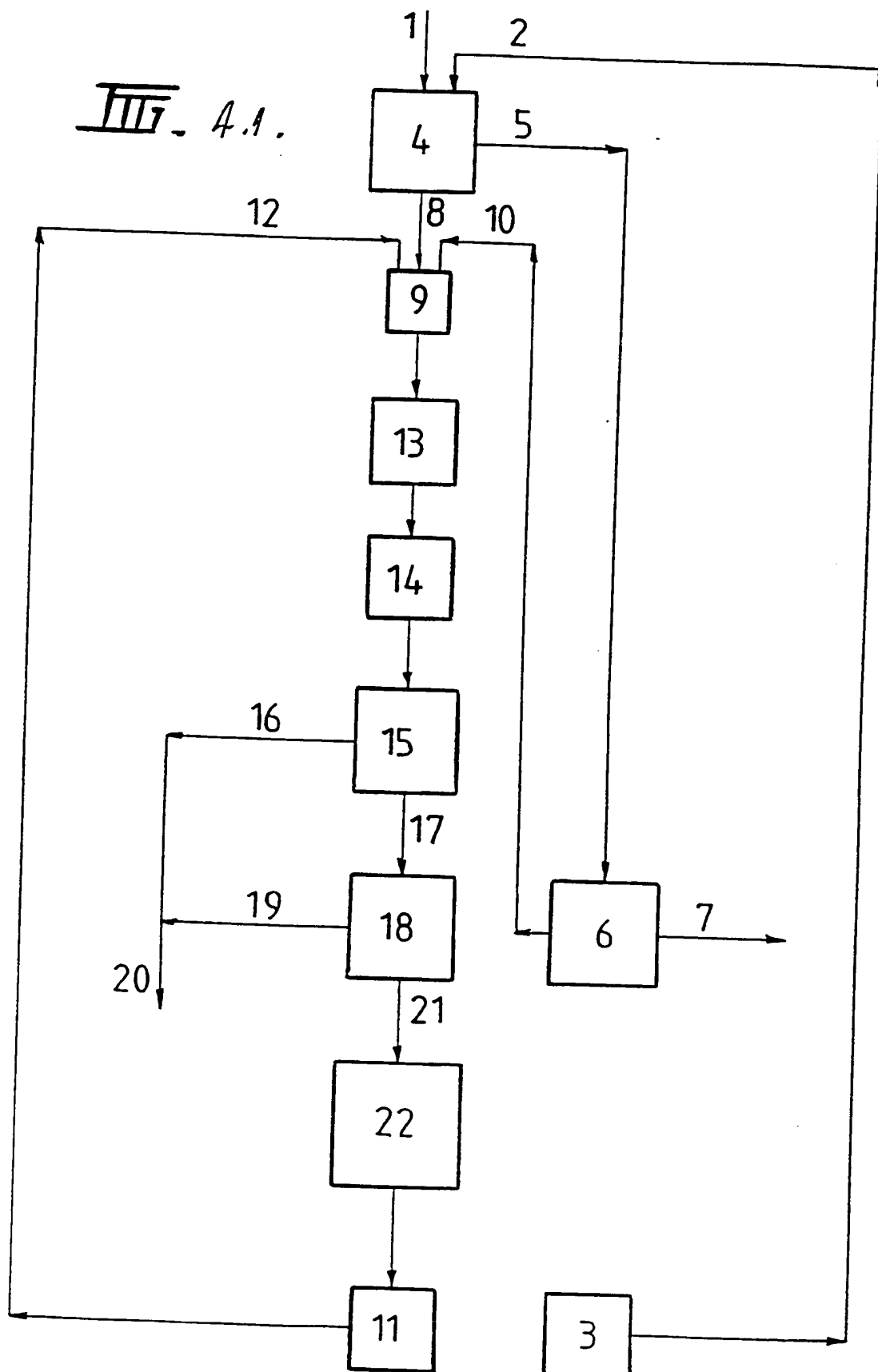


Figure 3.9

III 4.1.

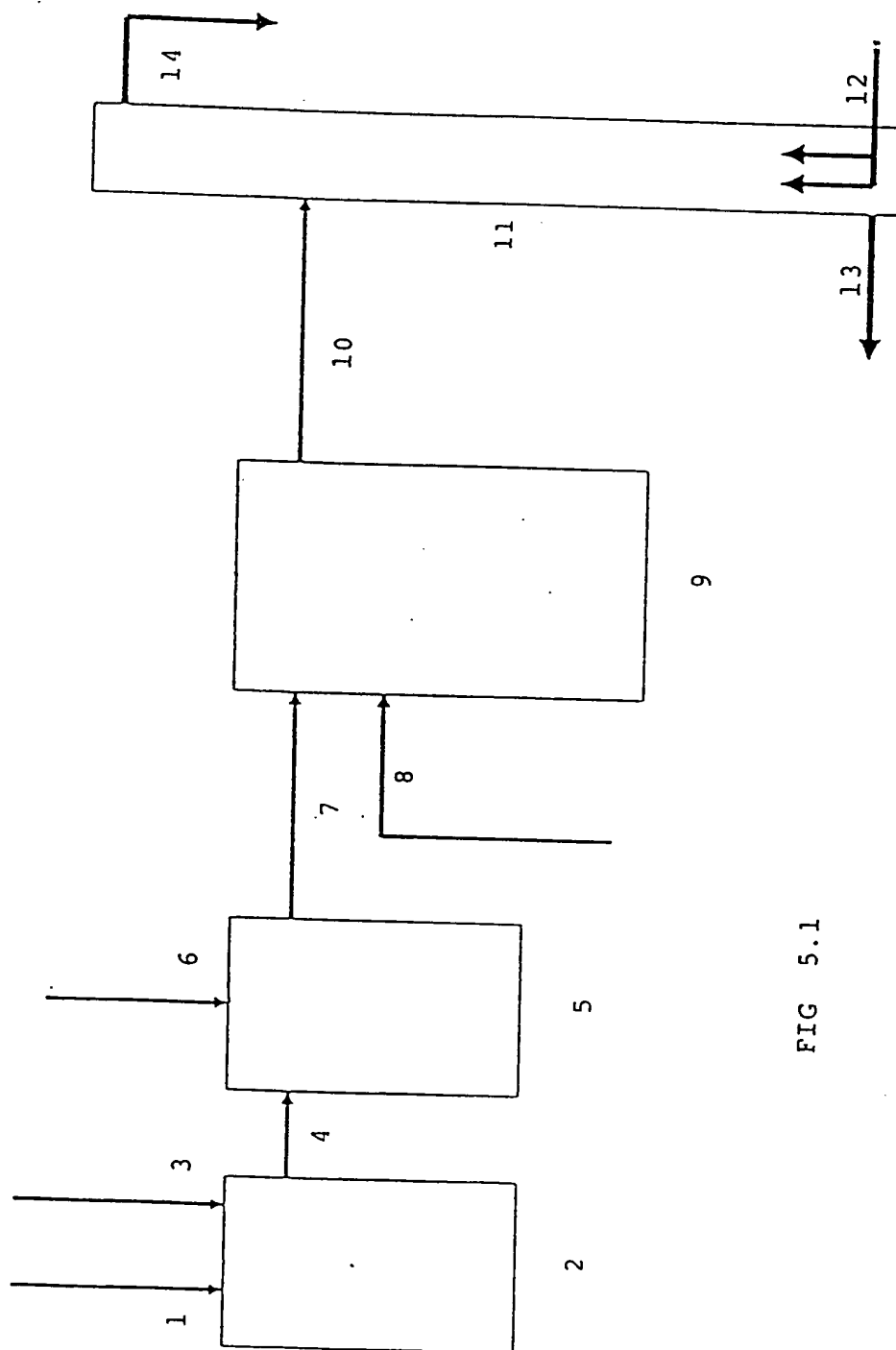


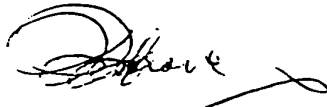
FIG 5.1

SUBSTITUTE SHEET

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/AU93/00076

<b>A. CLASSIFICATION OF SUBJECT MATTER</b> Int. Cl. <sup>5</sup> C02F 1/58; C02F 1/62; C02F 1/64;  According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b>  Minimum documentation searched (classification system followed by classification symbols) IPC C02F 1/58; C02F 1/62; C02F 1/64; C02C 5/02  Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched AU: IPC as above  Electronic data base consulted during the international search (name of data base, and where practicable, search terms used) DERWENT: Fatty ( ) Acid and [Sodium ( ) oleate or Na ( ) oleate or oleic ( ) Acid or Oleate]		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
X	Derwent Abstract Accession No. 18771Y/11, Class D15, JP,A,52-012763 (JAPAN CONS METAL PR) 31 January 1977 (31.07.77)	1-12
X	Derwent Abstract Accession No. 18772Y/11, Class D15, JP,A,52-012764 (JAPAN CONS METAL PR) 31 January 1977 (31.01.77)	1-12
X	Derwent Abstract Accession No. 87-319456/45, Class D15, SU,A,1293116 (ODESS UNIV) 29 February 1987 (29.02.87)	1-12
X	Derwent Abstract Accession No. 87-312498/44, Class D15, SU,A,1291549 (LENGD IND EFFL PURI) 23 February 1987 (23.02.87)	1-12
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
<b>* Special categories of cited documents :</b> "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed  "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search 10 May 1993 (10.05.93)		Date of mailing of the international search report 14 MAY 1993 (14.05.93)
Name and mailing address of the ISA/AU AUSTRALIAN PATENT OFFICE PO BOX 200 WODEN ACT 2606 AUSTRALIA  Facsimile No. 06 2853929		Authorized officer  J. BODEGRAVEN  Telephone No. (06) 2832281

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/AU93/00076

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate of the relevant passages	Relevant to Claim No.
A	Derwent Abstract Accession No. 91-315971/43, Class C04 D15 E14 (E35), SU,A,1627522 (RUBEZHAN DNEPR CHEM) 15 February 1991 (15.02.91)	1-12
A	Patent Abstract of Japan, C-331, page 4, JP,A,60-197294 (KOGYO GIJUTSUIN) 5 October 1985 (05.10.85)	1-12